The nitrogen hyperfine splitting constant is sensitive to the polarity of the microenvironment of the nitroxide spin label. Both labeled substrates exhibit the typical variation in this parameter as the medium is changed from highly polar aqueous to nonpolar hydrocarbon solution.[26] When either substrate is bound to the micelle or the polymer, the polarity experienced by the nitroxide is intermediate, but relatively polar, as observed in earlier studies on micelles.[23] Two patterns are observed. First, the polarity experienced by either label is greater in the polymer than in the micelle. This suggests that the substrates are less able to penetrate the nonpolar core of the polymer than that of the micelle. Second, the nitroxide group in the 5-doxylstearate experiences a less polar environment than that in the labeled testosterone in either polymer or micelle. It is not possible to specify unambiguously the cause of this difference. It is, however, consistent with a radial disposition of the 5-doxylstearate with the ionic headgroup located at the surface, forcing the polar nitroxide group a short distance into the interior.

In summary, the 5-doxylstearate appears to be "fixed" to the micelle, just as it is to the polymer, so the stearate tail seems to be located in an ordered, crystal-like region in the micelle interior. The labeled testosterone, on the other hand, experiences a more liquid-like micelle interior, although it too appears "fixed" to the polymer. It is possible, however, that the testosterone simply disrupts the order previously existing in the micelle. Both substrates are excluded somewhat more from the polymer core than from the micelle core. The covalent bonds apparently impose a higher degree of order than does the packing of the chains in the micelle. While this study does not provide a direct confirmation of the calculations of Dill and Flory,[6] all of the results obtained here are consistent with their general conclusions.

Conclusion

Poly(sodium 10-undecenoate), which is intuitively expected to have some of the characteristics of micelles in solution, has been shown to readily associate with amphiphilic and hydrophobic substrates. This establishes that a liquid-like core is not necessary for substrate binding. All of the results could be interpreted in a manner consistent with the recent conclusions of Dill and Flory[6] on the ordered interiors of micelles.

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Charge-Transfer Spectra of Metallophthalocyanines: Correlation with Electrode Potentials

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Abstract: Electrode potentials are reported for first-row transition-metal phthalocyanines for redox processes occurring both at the phthalocyanine ring and at the central metal ion. Procedures are developed for calculating the potentials of couples which cannot be directly observed. Electronic spectra are reported for many of these species and charge-transfer spectra identified. In many cases such absorption occurs at low energies in the near-infrared region. A model is developed to relate the electrode potentials with the observed charge-transfer spectra. This model provides an assignment for two allowed ligand-to-metal charge-transfer (LMCT) bands and affords calculated energies generally within 2000 cm^{-1}, of those observed. Both 0–0 and 1–0 vibrationally excited LMCT bands are observed. These data permit mapping of the electronic energies of metallophthalocyanines, allow determination of the redox energies of excited states, and hence lead to the purposeful design of metallophthalocyanines as solar energy conversion catalysts.

The phthalocyanine (Pc) ring is subject to successive one-electron oxidation or one-electron reduction to yield cation and anion radicals, respectively. The potentials at which these processes occur have been well documented.[1-6] With redox-active metals, metal oxidation or reduction may also occur. If one or more metal redox processes occur at potentials lying between the phthalocyanine oxidation and reduction, then we may infer that one or more metal d levels lie between the phthalocyanine HOMO (π) and LUMO (π^*) orbitals. In such circumstances metal-to-ligand (MLCT) and/or ligand-to-metal (LMCT) charge-transfer transitions may be observed.

Since the separation of the phthalocyanine ring HOMO and LUMO orbitals is only about 1.5–1.7 eV,[4] such charge-transfer transitions may lie at very low energies, probably in the near-infrared region. Fielding and MacKay have previously investigated this region in a number of metallophthalocyanines and report[7,8] weak transitions below 10000 cm^{-1} (1 eV = 8065 cm^{-1}) and ascribed to d–d bands or vibrational overtones. Fortuitously, they

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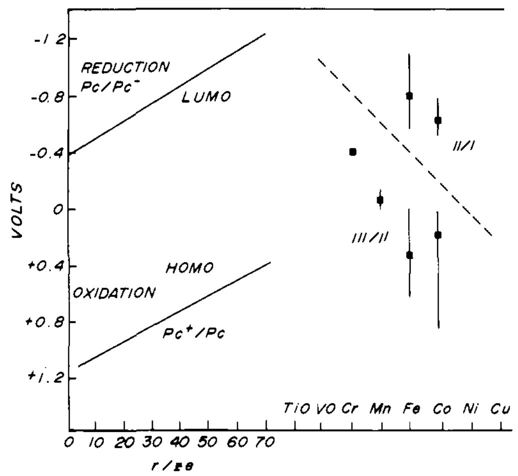

Figure 1. The left-hand side of the figure depicts the variation of main-group phthalocyanine LUMO and HOMO orbitals as a function of inverse polarizing power (radius/charge) (see ref 4 for details). The right-hand side depicts the variation of redox potentials for the III/II and II/I couples as a function of first-row transition-metal ion. In this fashion a qualitative picture emerges of which metal ions will possess d orbitals lying between the LUMO and HOMO orbital energies.

did not investigate species which, as shown here, exhibit intense charge-transfer absorption in this region.

Metallophthalocyanines enjoy growing importance as potential photocatalysts for energy conversion processes.[9,10] The presence of very low-lying charge-transfer states provides a mechanism for dissipating, in a nonuseful manner, most of the energy absorbed in the visible (solar) region. Hence an understanding of these charge-transfer processes will aid the design of future successful photocatalysts.

Such charge-transfer transitions are observed and are described here. Several metallophthalocyanines show beautifully rich near-infrared absorption. The charge-transfer energies and assignments can be correlated in a simple fashion with measured and estimated electrode potentials.

Experimental Section

The metallophthalocyanines were prepared and purified by standard literature techniques.[11-13] (Acetato)(tetra-*tert*-butylphthalocyanato)manganese(III)-1.5-water was prepared by reaction of manganese(II) acetate with unmetalated tetra-*tert*-butylphthalocyanine[12] in boiling dimethylformamide, followed by chromatography on silica. Anal. Calcd for $C_{50}H_{54}MnN_8O_{3.5}$: C, 68.4; H, 6.2; N, 12.8. Found: C, 68.9; H, 6.1; N, 12.1. The species is somewhat hygroscopic.

Trisodium (tetrasulfonato)(phthalocyanato)chromate(III) nonahydrate was prepared from chromium(II) acetate by following the general procedure of Weber and Busch.[13] It was purified by multiple chromatography on cellulose/water. Anal. Calcd for $C_{32}H_{34}CrN_8Na_3O_{12}S_4$: C, 34.4; H, 3.1; N, 10.0. Found: C, 34.75; H, 2.3; N, 9.9.

Electronic absorption spectra were recorded with a Perkin-Elmer Hitachi PE340 spectrometer. In this microprocessor instrument, the cuvettes and solvents are electronically matched to provide a base line against which the electronic spectra are recorded. Spectroanalytical solvents were used throughout.

Electrode potentials were determined by cyclic voltammetry (Princeton Applied Research Models 173, 174a, and 175), with procedures as reported previously.[2,4,6]

Discussion

In Figure 1 we illustrate schematically the range of energies over which main-group metallophthalocyanines are ring oxidized or ring reduced as a function of the polarizing power of the central metal ion.[4] These data provide approximate limits for ring reduction or oxidation and identify thereby the approximate positions of the HOMO and LUMO levels.

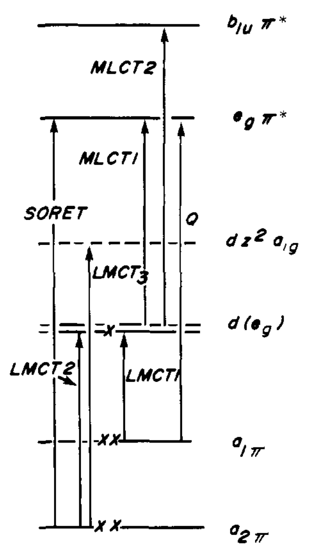

Figure 2. Scheme of the energy levels in a typical metallophthalocyanine, showing the origin of the various LMCT, MLCT, Q, and Soret bands discussed in the text.

The right-hand side of Figure 1 depicts the range of potentials over which first-row transition-metal phthalocyanines are reduced or oxidized at the central metal ion. Presumably because of increasing nuclear charge from left to right, these latter potentials also increase from left to right. However, note that variation of solvent and supporting electrolyte provides a wide range over which some potentials (such as PcFe(III)/PcFe(II)) can be observed.[2,14]

Of the metals studied, only chromium, manganese, iron, and cobalt exhibit redox processes at potentials lying within the HOMO–LUMO gap. These metal ions, Cr, Mn, Fe, and Co, should, therefore, exhibit LMCT transitions in accessible, relatively low-energy, regions of the spectrum. MLCT transitions might also be observed from these ions. Under some circumstances, other ions with deeper lying filled d orbitals may also exhibit charge-transfer spectra (see below).

General Theoretical Development. Most metallophthalocyanines belong to the point group D_{4h}.[11] According to the development of Gouterman and co-workers[15-18] the HOMO orbital is $a_{1u}(\pi)$ and the next low-lying filled orbital $a_{2u}(\pi)$. The LUMO is $e_g(\pi^*)$ (see Figure 2). Transitions from a_{1u} and a_{2u} to e_g are responsible for the two $^1E_u \leftarrow {}^1A_{1g}$ (π–π^*) transitions labeled as the Q band (13 300–16 500 cm^{-1}) (very strong) and Soret band (22 300–31 200 cm^{-1}) (strong) characteristic of the spectra of all metal phthalocyanine MPc(2−) species.[15-19] In addition, metallophthalocyanines exhibit one or two weaker bands near 16 500 cm^{-1} attributable to vibrational overtones of the Q band. Main-group (closed shell) phthalocyanines show no electronic bands other than these below about 33 000 cm^{-1}. In the UV region further π–π^* and n–π^* transitions, which generally will not concern us here will occur.[15-20]

Several metallophthalocyanines exhibit fluorescence (from the Q band) and/or phosphorescence from the ^3E_u state associated with the Q band. Such phosphorescence is commonly seen near 9500–10 500 cm^{-1}.[21-23] Absorption to the Q-band triplet, however,

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is strongly forbidden and is not observed.

With paramagnetic ions, coupling between the spin states on the metal and the phthalocyanine Q-band triplet state can occur to yield so-called "trip-multiplets" characterized in metalloporphyrin chemistry[24] but only briefly mentioned in metallophthalocyanine chemistry.[21] Investigation of possible charge-transfer transitions in transition-metal phthalocyanines was pioneered by Gouterman and co-workers[18,25] but no systematic study has been carried out.

We propose a model which electrode potentials may be used to estimate orbital energy levels and thus transition energies.

Consider a metal ion, such as M(III), possessing an empty d level into which a charge-transfer transition could occur from the filled $(a_{1u})^2$ phthalocyanine ring HOMO (see Figure 2, LMCT1). This transition may be written

$$\underset{\text{LMCT1}}{\mathrm{Pc(2-)(a_{1u})^2M(III)(d^n)} \rightarrow \mathrm{Pc(-)(a_{1u})M(II)d^{n+1}}} \tag{1}$$

The energy of LMCT1 clearly depends upon the ease of ring oxidation of Pc(2−)M(III) and the ease of metal reduction of this same species. We may write for these two processes

$$\mathrm{Pc(2-)(a_{1u})^2M(III)d^n + e^- \rightleftharpoons Pc(2-)(a_{1u})^2M(II)d^{n+1}} \quad E^\circ(\mathrm{Pc(2-)M(III)/Pc(2-)M(II)}) \tag{2}$$

and

$$\mathrm{Pc(2-)(a_{1u})^2M(II)d^{n+1} \rightleftharpoons Pc(-)(a_{1u})M(II)d^{n+1} + e^-} \quad -E^\circ(\mathrm{Pc(-)M(II)/Pc(2-)M(II)}) \tag{3}$$

which sum, with cancellation of electrons, to eq 1. Then the energy of LMCT1 may tentatively be written

$$\mathrm{LMCT1} = E^\circ(\mathrm{Pc(2-)M(III)/Pc(2-)M(II)}) - E^\circ(\mathrm{Pc(-)M(II)/Pc(2-)M(II)})\ \mathrm{eV} \tag{4}$$

and the corresponding equation for M(II) species

$$\mathrm{LMCT1} = E^\circ(\mathrm{Pc(2-)M(II)/Pc(2-)M(I)}) - E^\circ(\mathrm{Pc(-)M(I)/Pc(2-)M(I)})\ \mathrm{eV} \tag{5}$$

The second LMCT transition, LMCT2, originates from the a_{2u} orbital.[18] In phthalocyanine chemistry, in contrast to metalloporphyrin chemistry,[24] the a_{1u} and a_{2u} orbitals are sufficiently disparate in energy that mixing of the two ^1E_u states is minimized. Therefore we can approximate

$$E(a_{1u}) - E(a_{2u}) = E(\mathrm{Soret}) - E(\mathrm{Q}) \tag{6}$$

and therefore

$$\mathrm{LMCT2} = \mathrm{LMCT1} + E(\mathrm{Soret}) - E(\mathrm{Q}) \tag{7}$$

Similar equations may be written for the MLCT transitions, e.g., for the forbidden transition

$$\underset{\text{MLCT1}}{\mathrm{Pc(2-)(a_{1u})^2M(II)} \rightarrow \mathrm{Pc(3-)(a_{1u})^2(e_g)M(III)}} \tag{8}$$

we can sum

$$\mathrm{Pc(2-)(a_{1u})^2M(II)d^n \rightleftharpoons Pc(2-)(a_{1u})^2M(III)d^{n-1} + e^-} \quad -E^\circ(\mathrm{Pc(2-)M(III)/Pc(2-)M(II)}) \tag{9}$$

and

$$\mathrm{Pc(2-)(a_{1u})^2M(III)d^{n-1} + e^- \rightleftharpoons Pc(3-)(a_{1u})^2(e_g)M(III)d^{n-1}} \quad E^\circ(\mathrm{Pc(2-)M(III)/Pc(3-)M(III)}) \tag{10}$$

to yield

$$\mathrm{MLCT1} = E^\circ(\mathrm{Pc(2-)M(III)/Pc(3-)M(III)}) - E^\circ(\mathrm{Pc(2-)M(III)/Pc(2-)M(II)}) \tag{11}$$

Previous calculations lead to the conclusion that the energy separation between the e_g and b_{1u} π^* orbitals is about 1.4 eV;[14–17] we therefore estimate

$$\mathrm{MLCT2} = \mathrm{MLCT1} + 1.4\ \mathrm{eV} \tag{12}$$

There is an assumption implicit in this treatment that the metal d orbital from which, or to which, the electron moves, in the electrode process, is the same as that primarily utilized in the electronic transition. Where, as in most cases discussed here, t_{2g} (in O_h) orbitals are involved, selection rules require that the electronic transition involve the e_g (in D_{4h}) (xz, yz) orbitals. Should, in fact, the b_{2g} (xy) orbital be involved in the electrode process, the error will be small, since the splitting of the t_{2g} set should be small.

There are several other difficulties associated with this development. The electronic transition energy reflects a difference in *enthalpies* between the zeroth vibrational level of the ground state and an *excited vibrational* level of the excited electronic state, i.e., involves an excited state not necessarily in its equilibrium nuclear configuration. The sum of the electrode potentials reflects a difference in *free energy* between two species primarily in their vibrational (zeroth) ground states.

As we show below, the charge-transfer states are 0–0 in vibrational characteristic so this potential source of error disappears. The enthalpy and free energy differences will be the same if the entropy difference between the states concerned is zero. Because of the rigidity of the molecule and the tendency in most cases to remain six-coordinate, the entropy differences between the various components of these couples may indeed be small. The removal or addition of one electron from a 32π-electron system[11] is not expected to have much effect on the molecular structure.

Equations 4, 5, and 7 provide a remarkably good approximation to the charge-transfer energies, implying that the concerns mentioned immediately above do not seriously vitiate the use of these equations. Previous studies showed most satisfactory relationships between charge-transfer absorption and redox data when species of similar entropy were compared.[26,27] Clearly, such a development should be used with caution; it does seem to be valid here.

All the relationships between electronic transition energies and electrode potentials involve differences in the latter. For this reason it is irrelevant which reference electrode is used to record data. More significantly, any junction potentials will also cancel out, provided only that all data for a given system are collected against the same reference electrode (SCE in this case) and in the same solvent. It is not necessary to correct the charge-transfer transition energies for changes in mean spin repulsion energy because such energies are included within the electrode potentials. Moreover, solvation energy contributions to the electrode potentials will similarly influence charge-transfer state energies and therefore be automatically corrected for in the treatment.

Experimental Electronic Spectrscopic Data. Titanyl and Vanadyl Phthalocyanines. No charge-transfer bands are predicted at energies below the Soret band, and indeed no bands in addition to the Q and Soret bands are observed between 6250 and 33 300

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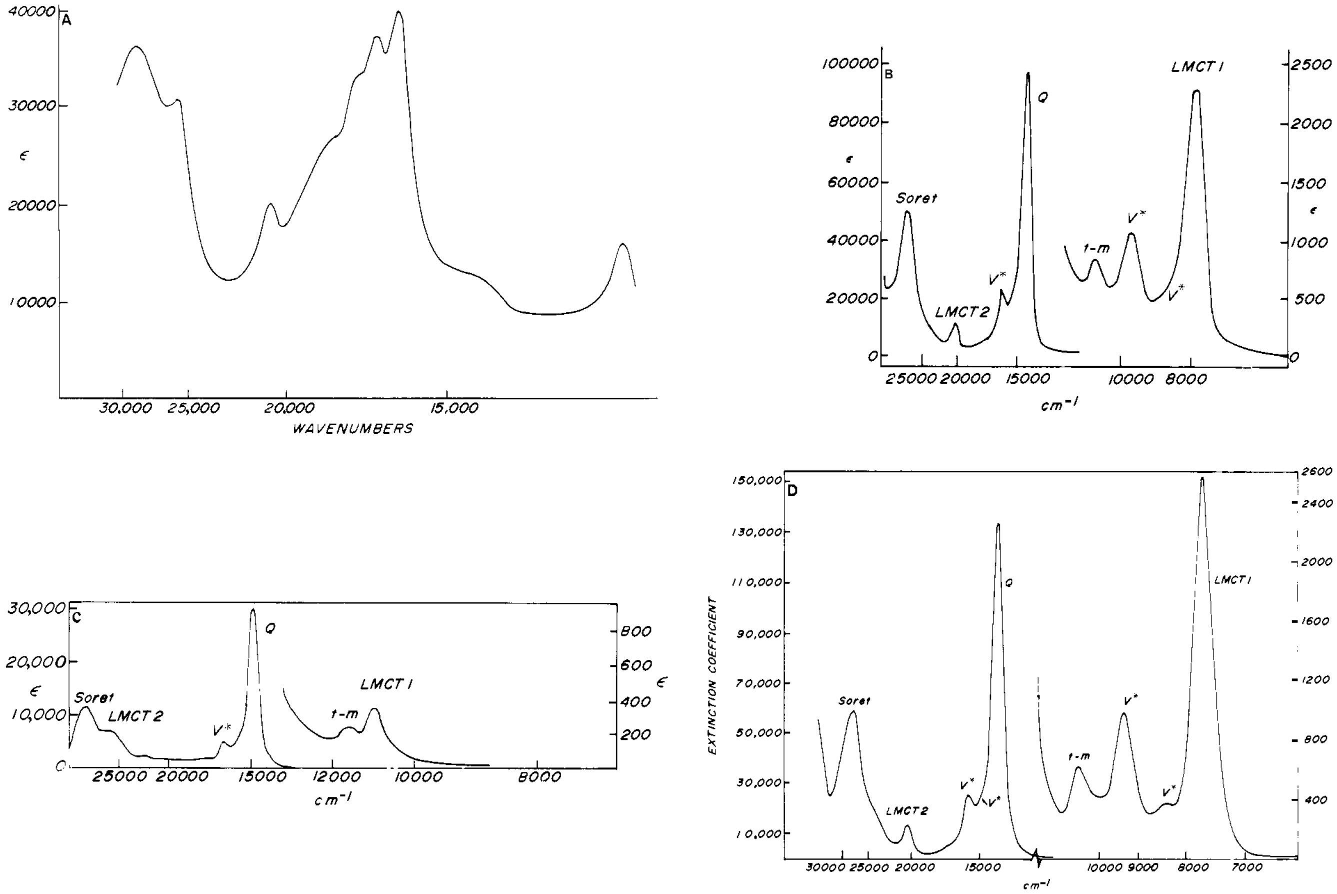

Figure 3. Electronic spectra of chromium and manganese phthalocyanines dissolved in dimethylformamide (range 6000–33 000 cm^{-1}): (A) TsPcCr(II) prepared by electrochemical reduction of Na$_3$TsPcCr(III) at a platinum electrode (at -0.7V vs SCE)[48] (the shoulder near 15 000 cm^{-1} arises from a chromium(III) impurity in this highly air-sensitive complex); (B) Na$_3$TsPcCr(III); (C) PcMn(II)(Et$_3$N)$_2$; (D) (t-Bu)$_4$PcMn(III)OAc. Note that both the wavelength and intensity scales change between the visible and near-infrared regions in B, C, and D.

cm^{-1}. The vanadyl system should exhibit weak d–d transitions but these have not been identified.

Chromium Phthalocyanines. The spectra of several chromium(II) and chromium(III) phthalocyanines are shown in Figure 3A,B. Additional absorption bands of moderate to high intensity are observed both in the near-infrared region and at energies lying between the Soret and Q bands. In view of the large crystal field splitting of the phthalocyanine group, we do not expect any spin-allowed d–d bands to occur in the near-infrared region for the chromium(III) d^3 species and the "extra" visible bands are too intense to be so identified.

Let us consider that these "extra" transitions are charge transfer in origin. Selection rules require that only the transitions a_{1u} or $a_{2u} \rightarrow e_g(d)$ (LMCT1, LMCT2) and $a_{2u} \rightarrow a_{1g}d_{z^2}$ (LMCT3) are permitted for electric dipole radiation. Moreover, LMCT1 should be less intense than LMCT2.[18] The a_{1u} orbital has a node at the chelating nitrogen atoms and the overlap between ground and excited states of LMCT1 will therefore be small. Indeed this is seen to be the case below.

The chromium(III) species will have a hole in the $e_g(d_\pi)$ orbital; the appearance of the relevant LMCT bands in the chromium(II) spectra requires that these low-spin d^4 species also have a hole in $e_g(d_\pi)$. The relevant equations to calculate their energies, based upon eq 4 and 5, are

Chromium(II)

$$\text{LMCT1} = E^\circ(\text{Pc(2–)Cr(II)/Pc(2–)Cr(I)}) - E^\circ(\text{Pc(–)Cr(I)/Pc(2–)Cr(I)}) \quad (13)$$

Chromium(III)

$$\text{LMCT1} = E^\circ(\text{Pc(2–)Cr(III)/Pc(2–)Cr(II)}) - E^\circ(\text{Pc(–)Cr(II)/Pc(2–)Cr(II)}) \quad (14)$$

with LMCT2 defined by eq 5.

Table I. Observed and Estimated Redox Data[a]

couple	TsPcCr	PcMn	average
Pc(–)M(I)/Pc(2–)M(I)	0.39[b]	0.39[b]	0.39[b]
Pc(–)M(II)/Pc(2–)M(II)	0.72[b]	0.72[b]	0.72[b]
Pc(2–)M(IV)/Pc(2–)M(III)	1.00[c]	0.80[c]	
Pc(2–)M(III)/Pc(2–)M(II)	–0.40	–0.14 (a)	
Pc(2–)M(II)/Pc(2–)M(I)	–1.00	–0.88	
Pc(2–)M(IV)/Pc(3–)M(IV)			–0.54
Pc(2–)M(III)/Pc(3–)M(III)			–0.70
Pc(2–)M(II)/Pc(3–)M(II)	–1.00	–0.69 (b)	–0.85
Pc(2–)M(I)/Pc(3–)M(I)			–1.18

[a] Volts vs. SCE. [b] Average potentials are those for first-row transition-metal metallophthalocyanines in given oxidation state.[28] Corresponding oxidation potentials are estimated by adding 1.57 V to these figures.[4] Electrochemical data refer to DMF solution with tetraethylammonium perchlorate as supporting electrolyte (ref 2, 4, 14, and this work). [c] Estimate: (t-Bu)$_4$PcMn(III)OAc, (a) = –0.11 V, (b) = –0.89 V.

Not all the necessary couples can be directly observed; e.g., in the sequence of oxidations Pc(2–)Cr(II) → Pc(2–)Cr(III) → Pc(–)Cr(III) a redox couple arising from direct oxidation of a phthalocyanine ring containing chromium(II) cannot be observed and must be estimated.

In Table I are are listed redox potentials for a series of mono-, di-, tri-, and tetravalent Mn and Cr phthalocyanines. Some of these were directly measured,[1-6,14] while others were estimated from a detailed survey of the electrochemical potentials of metallophthalocyanines.[28] Such an estimate is unlikely to be in error by more than about 200 mV, representing a band transition energy error of about 1600 cm^{-1}, certainly acceptable agreement.

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Before we calculate these charge-transfer energies, we note that the following requirements should identify these bands in the spectra: (a) LMCT bands in the M(III) spectra should be red shifted relative to the corresponding bands in the corresponding M(II) complexes; (b) LMCT1 and LMCT2 should be identifiable in the spectra as a pair of bands separated by approximately the same energy as the Soret and Q bands; (c) LMCT1 should be less strong than LMCT2.

Indeed such bands can be identified (see Figure 3), some in the near-infrared region. The absence of such near-infrared absorption in iron, nickel, or copper TsPc complexes in DMA precludes the possibility that these spectra are artifacts or are phthalocyanine or solvent vibrational overtones.

Using eq 13 and 14 and the data in Table I, we can calculate their energies; these results are compared with observed data in Table II. The agreement is remarkably good. The successful prediction of the relative band intensities, band separation, and absolute band energies of these absorption features can leave no doubt that they are correctly identified as LMCT1 and LMCT2.

The LMCT1 transition in the chromium(II) derivative is remarkably intense when compared with other LMCT1 transitions discussed below. Moreover, the Q band in chromium(II) lies at an unusally high energy and is weaker than usual for Q bands. It seems probable that there is extensive mixing between the Q and LMCT1 transitions in the chromium(II) species because they lie fairly close together, resulting in both the blue shift in the Q band and in the unusual intensity distribution.

The band at 19 650 cm^{-1} in the chromium(II) complex is conceivably MLCT2 or LMCT3 (see Figure 1). The MLCT2 transition terminates in the b_{1u} orbital, which has a node on the chelating nitrogen atoms,[11] so the intensity of the MLCT2 transition is expected to be low.[16] Moreover, metal-to-ligand charge-transfer bands are generally weaker than ligand-to-metal charge-transfer bands.[29,30] Therefore it is unlikely that this rather strong band could be assigned to MLCT2. Moreover, the calculated position of MLCT2 (Table I) is much lower in energy than 25 000 cm^{-1}, in a position where, if it is indeed very weak, it would assuredly be hidden by the O band.

The energy of the LMCT3 transition is approximately equal to the Q band–Soret band separation plus the energy separation between the t_{2g} (in O_h) orbitals and the $a_{1g}d_{z^2}$ orbital. if the 19 650-cm^{-1} band is assigned to LMCT3, then this d-orbital separation must be about 6000 cm^{-1}, which for a tetragonally distorted molecule–divalent metal complex is not unreasonable. Tentatively, we assign the 19 650-cm^{-1} band to LMCT3. Proof may be obtained, in due course, through MCD experiments.

We discuss the remaining extra bands in these spectra during the discussion of manganese species below.

Manganese Phthalocyanines. Pairs of charge-transfer absorption with appropriate separation and relative intensity are also observed in the manganese(II) and manganese(III) phthalocyanine spectra (Figure 3C,D). The latter has especially rich near-infrared spectra red shifted relative to manganese(II). The manganese(III) spectra are strongly reminiscent of the chromium(III) spectra, for reasons which will be explored below. The manganese(III) complexes are high-spin d^4 and therefore possess a hole in $e_g(d_\pi)$. The complex Pc(2−)Mn(II)$(Et_3N)_2$, whose spectrum is reported here, is a low-spin d^5 species.[31] The observation of LMCT1 and LMCT2 requires that the hole must be in the $e_g(d_\pi)$ orbital. In a pure DMF solution of Pc(2−)Mn(II), freed from contaminating dimethylamine, no bands are observed in the near-infrared region. Such a solution does not contain low-spin manganese(II).[32] The anticipated LMCT band may have blue shifted under the Q-band absorption.

Table II. Observed and Calculated Data: Chromium and Manganese Data (cm^{-1})

complex	obsd (intensity)	*P*	assignment	calcd
	Chromium(II)			
TsPc	11 850 (16 600)		LMCT1	11 210
	?		MLCT2	13 710
	16 300 (41 000)		Q band	
	17 000 (38 000)		?[a]	
	17 600 sh		Q–(1–0)V*	
	18 400 sh		?	
	20 800 (20 600)		LMCT3?	
	25 900 (31 200)		LMCT2	24 110
	29 200 (33 800)		Soret	
	Chromium(III)			
$TsPcNa_3$	7 900 (2292)	0.0053	LMCT1	9 030
	8 550 sh		LMCT1–(1–0)V*	
	9 625 (1076)	0.0032	LMCT1–(1–0)V*	
	10 965 (845)	0.0019	trip-mul	
	14 370 (97 450)	0.19	Q band	
	15 060 sh		Q–(1–0)V*	
	15 975 (22 950)		Q–(1–0)V*	
	20 080 (11 450)	0.054	LMCT2	22 750
	?		MLCT2	23 710
	28 090 (50 240)	0.86	Soret	
	Manganese(II)			
PcMn(II)-$(Et_3N)_2$	10 910 (350)		LMCT1	10 240
	11 600 (230)		trip-mul	
	14 890 (30 000)		Q band	
	15 600 sh		Q–(1–0)V*	
	?		MLCT2	15 810
	17 200 sh		Q–(1–0)V*	
	26 300 (6600)		LMCT2	25 450
	30 100 (11 400)		Soret	
	Manganese(III)			
$(t\text{-Bu})_4$-PcMn(III)-OAc				
	7 630 (2574)	0.0049	LMCT1	6 935
	8 335 (444)		LMCT1–(1–0)V*	
	9 310 (1193)		LMCT1–(1–0)V*	
	10 670 (757)	0.0033	trip-mul	
	13 970 (134 400)	0.34	Q band	
	14 665 sh		Q–(1–0)V*	
	15 505 (25 100)		Q–(1–0)V*	
	20 120 (12 000)		LMCT2	20 140
	?		MLCT2	22 100
	23 810 sh		n–π*?	
	27 175 (58 600)	0.93	Soret	

[a] See ref 48. All data recorded in DMF solution. Intensities reported as L mol^{-1} cm^{-2}. The chromium(III) data were recorded with the trisodium salt of TsPcCr(III). The chromium(II) data were obtained by electrochemical reduction of this solution at a platinum electrode. (1-0)V* signifies excitation to a first vibrational overtone level of the excited electronic state. trip-mul signifies a trip-multiplet transition. *P* = oscillator strength based on standard molar extinction coefficient, half-bandwidth equation.[29]

Only the Pc(2−)Mn(III)/Pc(2−)Mn(II) couple can be directly observed;[6] the other required couples (according to eq 4 and 5) are estimated[28] to yield the calculated charge-transfer data shown in Table II, in excellent agreement with experiment.

Three bands lie between LMCT1 and the Q band in both the chromium(III) and manganese(III) spectra. It is conceivable that, in the manganese(III) spectrum, one or more of these bands are d–d in origin.[29] However, this could not be the case for the chromium(III) spectra; they are too low in energy. Since the band envelopes and spacings between the bands are so similar in both the Cr(III) and Mn(III) spectra, we consider it more likely that the assignments must be the same for both species, ruling out, thereby, a d–d mechanism.

Consideration of Figure 3 (parts B and D) reveals close similarity between the pattern of the first three near-infrared bands (strong (LMCT1), very weak, medium, reading to increasing

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(32) No ESR spectrum typical of low-spin manganese(II) can be detected in a DMF solution of Pc(2−)Mn(II) freed from contaminating dimethylamine.

energy) and the pattern in the Q-band region (strong, weak (or shoulder), medium). The extra bands on the high-energy edge of the Q bands are excitations to vibrationally excited $e_g(\pi^*)$ levels; i.e., the Q band is a 0–0 transition while the weaker bands 500–1700-cm^{-1} to higher energy are transitions of the 1–0 vibrational type.[24] The separations between the first three near-infrared bands (including the very weak band some 500 cm^{-1} above LMCT1) are, to within 100 cm^{-1}, the same as the separations between the three transitions in the immediate vicinity of the Q band.

Moreover, the LMCT bands are remarkably narrow. Their half-bandwidths vary from as low as 378 cm^{-1} for LMCT1–Cr(II), through, for example, 405 cm^{-1} (LMCT1–Mn(III)), 552 cm^{-1} (LMCT1–Cr(III)), and 880 cm^{-1} (LMCT2–Cr(III)). LMCT2–Cr(II) is also very narrow but its closeness to the Soret band renders it difficult to measure. It seems likely that these transitions are indeed 0–0 bands in vibrational nature, though this is unexpected for LMCT transitions which involve changes in oxidation level. However, note that, for LMCT1, excitation is from a ligand orbital which has a node at the nitrogen atoms and therefore will have little effect upon the σ binding energy. Perhaps in these fairly rigid macrocycles there is very little difference in bond length between M(II) and M(III) species etc. We are not aware of any X-ray data yet available for a given metal phthalocyanine in several oxidation states.

We conclude that the two bands immediately following LMCT1 are vibrationally excited LMCT1 transitions. It is valid to note that their intensities, relative to the 0–0 band, are farily high, proportionately much higher than the corresponding vibrational components of the Q band. This may be taken as evidence of anharmonicity.

There remains assignment of the band near 10600–11600 cm^{-1} in some of these complexes. The intensity and position of this transition closely parallel those of the trip-multiplet transition unequivocally assigned in the copper spectrum (below). It is therefore so assigned. The additional peak, in this same region, in the manganese(II) spectrum is also likely to be trip-multiplet in origin.

We have found no evidence in either the chromium or manganese spectra for the allowed MLCT2 transition, whose calculated energy is also displayed in Table II.

Iron Phthalocyanines. Mononuclear iron(III) phthalocyanines have rarely been identified. However, they can be obtained in the tetrasulfonated form, TsPcFe(III),[13] and in binuclear μ-oxo species.[33,34] We were unable to discover any charge-transfer absorption in the near-IR region with either the mononuclear or the μ-oxo iron(III) species. Presumably the $e_g(d_\pi)$ level is filled. Schaffer et al.[18] consistently calculate $e_g(d_\pi)$ below $b_{2g}^*(xy)$, probably thereby explaining why the former is filled.

Square-planar iron(II) phthalocyanine is reported[20] to possess a weak band near 12200 cm^{-1} in dichlorobenzene solution. This absorption has been assigned[20] as a $^3E_u \leftarrow {}^3A_{2g}$ MLCT transition arising from $e_g(d_\pi) \rightarrow b_{1u}(\mathrm{Pc}\ \pi^*)$ (MLCT2). On the basis of eq 12 and with a Pc(2−)Fe(III)/Pc(2−)Fe(II) energy of 0.19 V,[2] this transition, which should be very weak, should appear near 18500 cm^{-1}. On the other hand, the $^3E_u \leftarrow {}^3A_{2g}$ transition originating from $a_{1u} \rightarrow e_g(d)$ (LMCT1) (not considered by the previous workers[20]) should lie in the region of 12000 cm^{-1}, depending upon the Fe(II)/Fe(I) couple energy in this medium. Such an assignment is consistent with the MCD data[20] and is considered more likely than the previous assignment.

Low-spin iron(II) phthalocyanines ($e_g^4b_{2g}^2$) do not possess a hole in their e_g level and therefore do not exhibit low-energy LMCT transitions. However, these species often show a band in the 20000–25000-cm^{-1} region, variously assigned as a ML-(axial)CT (in Pc(2−)Fe(II)(pyridine)$_2$[18,35]) and as an internal phthalocyanine transition.[20] The $a_{2u} \rightarrow a_{1g}(d_{z^2})$ LMCT3 transition is anticipated to lie in this general region. However, the MCD data do not support this assignment, and the band apparently moves to lower energy with increasing donor strength of the axial ligand;[20,25] both these observations appear to refute the LMCT3 assignment. We note that this band can be observed with iron(II) phthalocyanines dissolved in DMA (DMA as axial ligand) and in the presence of triethylamine (Et_3N as axial ligand). In neither case will the axial ligand have a suitable acceptor orbital; hence a charge-transfer assignment to the axial ligand is eliminated. The identity of this absorption band therefore remains in doubt.

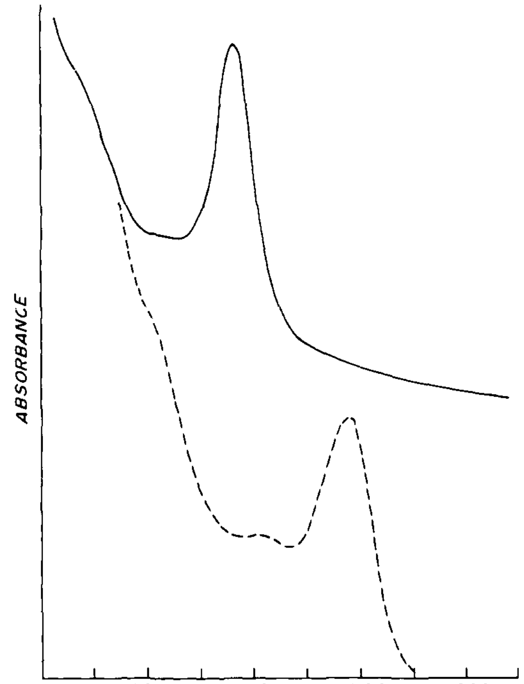

Figure 4. Doublet–quartet transitions near 10000 cm^{-1}: (upper) PcCo(II)(pyridine)$_2$ dissolved in pyridine (10245 cm^{-1} (1210)); (lower) TsPcCu(II) dissolved in dimethyl sulfoxide (9250 cm^{-1} (99)). TsPcNi(II) exhibits no absorption in this region.

Cobalt Phthalocyanine. Cobalt(II) phthalocyanines are usually observed as five- or six-coordinate low-spin species. Several workers have noted near-infrared absorption consisting of broad bands in the 4000–7000-cm^{-1} range and a sharper, stronger absorption near 10000–11000 cm^{-1}.[36-39] Most of these bands have been assigned as d–d transitions. Since the e_g level is filled, only LMCT3[18] can theoretically be observable. This transition should appear near 10000 cm^{-1}, depending upon the nature of the axial ligands.

In Figure 4 is shown the spectrum of six-coordinate Pc(2−)-Co(II)(pyridine)$_2$, which, as would be anticipated, does not show any low-energy bands of d–d origin but does show sharp absorption at 10245 cm^{-1}. This band has previously been assigned as a d–d transition,[35] but it is doubtful that this is the case.

We note that the shape, position, and intensity of this transition are very similar to those of corresponding bands in manganese, chromium, and especially copper phthalocyanines, which also have $S = {}^1/_2$. These bands are assigned as trip-multiplets. We therefore prefer this assignment but plan further studies of the variation of this band as a function of axial ligand in order to positively identify its nature.

Nickel(II) Phthalocyanine (Square-Planar Low-Spin d^8). No LMCT transitions from phthalocyanine a_{1u} or a_{2u} levels are permitted, and no absorption other than the anticipated π–π^*

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transitions are observed at energies below the Soret band. Gouterman and co-workers[18] assign a series of additional bands starting at 35 200 cm^{-1} to MLCT $e_g(d) \rightarrow b_{1u}(\pi^*)$ and to higher π^* levels. Using our model, with the Pc(2−)Ni(III)/Pc(2−)Ni(II) couple guesstimated to lie at 1.5 eV, we estimate the MLCT2 transition (eq 12) to lie somewhat above 29 000 cm^{-1}, depending upon the energy separation between the $e_g(d)$ level and higher filled d-orbital levels. This is in satisfactory agreement with the assignment of Gouterman.[18]

Copper(II) Phthalocyanine (Square-Planar d^9). No LMCT transitions are permissible from a_{1u} or a_{2u}. However, copper(II) does show near-infrared absorption with a sharp peak near 8300 cm^{-1}, observed initially in its crystal spectrum.[40] Interestingly, copper(II) phthalocyanine is photoconductive in this near-infrared region.[41-45]

We report the first solution spectrum of copper(II) phthalocyanine (Figure 4) showing this absorption band, which must be a trip-multiplet transition[21] since no other options are available for this ion. The similarity between this absorption spectrum band envelope and that of the near-infrared photocurrent action spectrum[45] is astonishing. Note that inelastic electron tunneling spectroscopy has been used to determine electronic transitions in a range of metallophthalocyanines and that transitions were observed at 1.23 and 1.15 eV for CoPc and CuPc, respectively, in close agreement with the absorption data reported here.[46]

Conclusions

The electrochemical model and the energy level diagram shown in Figure 2 provide a convincing interpretation of the charge-transfer spectra of first-row transition-metal phthalocyanines. The errors associated with variation in entropy from ground to excited state and the vibrational excitation of the excited state appear to be small, or to cancel, to provide remarkable agreement between observed and calculated band energies. Indeed as discussed above the apparent 0–0 nature of the LMCT bands eliminates the vibrational excitation error.

These data are important because they provide a detailed and quantitative understanding of the lower excited states of metallophthalocyanines which may ultimately find use as photocatalysts.[10] In particular, acceptance of the model allows the electronic spectra to be used as a means of calculating excited-state potentials simply by reversing the procedure outlined in this paper.[10] They are also relevant to studies in electron transfer in metalloproteins, providing parallel data to some recent studies on heme porphyrin charge-transfer spectra by Makinen and coworkers.[46]

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(48) The spectrum reported in Figure 3A is the spectrum initially observed after electrochemical reduction of the chromium(III) starting material. It shows evidence of aggregation since it appears to exhibit two Q bands. After some period of time the two bands are replaced by a single Q band at an energy approximately midway between the two Q bands and with an intensity approximately twice their value. There are some concomitant changes in the cyclic voltammogram with time. We hope to provide further data on this system in due course. There is the possibility that the band near 28 000 cm^{-1}, identified as LMCT2, may possess some Soret character.

Electroreductive Alkylation of Iron in Porphyrin Complexes. Electrochemical and Spectral Characteristics of σ-Alkyliron Porphyrins

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Abstract: σ-Alkyliron porphyrins can be obtained by the reaction of electrogenerated iron(I) porphyrins on alkyl halides. The $(Fe^{II})^{-}R$ complex thus obtained can be oxidized electrochemically in a reversible manner into the corresponding complex $(Fe^{III})^{-}R$. The latter undergoes a further one-electron oxidation into a transient (formal) $(Fe^{IV})^{-}R$ complex. The UV–visible spectra of both the $(Fe^{III})^{-}R$ and $(Fe^{II})^{-}R$ porphyrins have been obtained. ESR and NMR spectra of the $(Fe^{III})^{-}R$ porphyrins show that they are low-spin complexes involving a σ-iron–carbon bond. The standard potentials of the $(Fe^{III})^{-}R/(Fe^{II})^{-}R$ couple shift negatively, parallel to those of the Fe(II)/Fe(I) couple, as the porphyrin ring becomes more electron donating. In all cases, opposite to what occurs with cobalt porphyrins, the former potential is positive to the latter, indicating a better affinity of R· toward Fe(I) than toward Fe(II). The reactivity of the iron(I) porphyrins toward RX increases with the electron-donating ability of the ring. The reaction mechanism appears more likely to be of the S_N2 type than to involve prior outer-sphere electron transfer between Fe(I) and RX.

The synthesis of metal-σ-alkyl derivatives of tetraazamacrocyclic cobalt complexes is presently a well-documented area. These derivatives can be prepared according to three different types of reactions: carbanion transfer to Co(III) from another organometallic compound, usually Grignard or organolithium reagents;[2] addition of the alkyl radical to Co(II), the Co(II) complex generating the alkyl radical through halogen abstraction from the starting alkyl halide,[3] nucleophilic attack of the Co(I)

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