

**Figure 1.** Carbon 1s spectrum of  $\text{Cr}(\text{CO})_5\text{CNCF}_3$ . The primary, low binding energy peak is due to the CO groups and the isocyano carbon atom; the broad high binding energy peak is due to shake-up and the  $\text{CF}_3$  carbon atom.

rically<sup>23</sup> measured value of  $-23.7 \text{ kcal mol}^{-1}$ . In a completely analogous way, we use the carbon binding energies of  $\text{CF}_3\text{NC}$  and  $\text{CF}_3\text{CN}$  to calculate the value  $-23 \text{ kcal mol}^{-1}$  for the  $\text{CF}_3\text{NC} \rightarrow \text{CF}_3\text{CN}$  isomerization energy. This value is in remarkably good agreement with the value  $-22.8 \text{ kcal mol}^{-1}$  calculated by the MNDO method.<sup>4</sup>

#### Experimental Section

Trifluoromethyl isocyanide was prepared by the reduction of  $\text{CF}_3\text{NCCl}_2$  over Mg.<sup>2</sup> The vapor pressure at  $-126^\circ\text{C}$  (methyl cyclohexane slush) was 66.1 mm and did not vary with the quantity of sample vaporized. The infrared spectrum agreed with that in the literature.<sup>2</sup>

Pentacarbonyl(methyl isocyanide)chromium was prepared by the reaction of  $[\text{N}(\text{CH}_3\text{CH}_2)_4][\text{Cr}(\text{CO})_5\text{I}]$  with  $[(\text{CH}_3\text{CH}_2)_3\text{O}][\text{BF}_4]$  in the

(23) Baghal-Vayjooee, M. H.; Colister, J. L.; Pritchard, H. O. *Can. J. Chem.* **1977**, *55*, 2634.

presence of  $\text{CH}_3\text{NC}$ .<sup>24</sup> The compound was purified by sublimation, and its melting point,  $68^\circ\text{C}$ , agreed with the literature value.<sup>25</sup>

The chromium and tungsten pentacarbonyl complexes of trifluoromethyl isocyanide were prepared by a literature procedure.<sup>5</sup> Trifluoroacetonitrile was a gift from Prof. J. Shreeve, University of Idaho.

Vapor-phase X-ray photoelectron spectra were obtained on a GCA/McPherson ESCA 36 spectrometer with a Mg anode. The method used for obtaining the calibrating spectra has been described previously.<sup>26</sup> The flow of trifluoromethyl isocyanide and trifluoroacetonitrile into the spectrometer was regulated with a needle valve. The trifluoromethyl isocyanide was held at  $-126^\circ\text{C}$  during data collection to prevent polymerization. The organometallic compounds were sublimed directly into the spectrometer from a sample reservoir held at  $10^\circ\text{C}$  through a large-diameter (1.5 cm) inlet system.

The C 1s spectrum of both the chromium and tungsten pentacarbonyl complexes of trifluoromethyl isocyanide showed two well-separated peaks (Figure 1). We have assigned the narrower peak (fwhm  $\approx 1.5 \text{ eV}$ ) at lower binding energy to the CO carbon atoms and the isocyano carbon atom of  $\text{CNCF}_3$ . The broad peak (fwhm  $> 3 \text{ eV}$ ) at higher binding energy is a composite of the peak due to the  $\text{CF}_3$  carbon atom and CO shake-up. The shake-up peak/primary peak intensity ratios, after correction for the contributions to the shake-up peaks of the  $\text{CF}_3$  carbon atoms, were 0.63 and 0.38 for  $\text{Cr}(\text{CO})_5\text{CNCF}_3$  and  $\text{W}(\text{CO})_5\text{CNCF}_3$ , respectively. These intensity ratios may be compared with the values 0.38 and 0.27 for the comparable bands of  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , respectively.<sup>27</sup>

**Acknowledgment.** This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract No. DE-A003-76SF00098. We thank Professor J. Shreeve for the sample of  $\text{CF}_3\text{CN}$ .

**Registry No.**  $\text{CF}_3\text{NC}$ , 19480-01-4;  $\text{Cr}(\text{CO})_5(\text{CNCF}_3)$ , 88902-50-5;  $\text{W}(\text{CO})_5(\text{CNCF}_3)$ , 88902-51-6;  $\text{Cr}(\text{CO})_5\text{CNCN}_3$ , 33726-04-4;  $\text{CF}_3\text{CN}$ , 353-85-5.

(24) Higginson, B. R.; Lloyd, D. R.; Burroughs, D. M.; Gibson, D. M.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1659.

(25) Connor, J. A.; Jones, E. M.; McEwen, G. K.; Lloyd, M. K.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1971**, *12*, 1246.

(26) Chen, H. W.; Jolly, W. L.; Kopf, J.; Lee, T. H. *J. Am. Chem. Soc.* **1979**, *101*, 2607.

(27) Bancroft, G. M.; Boyd, B. D.; Creber, D. K. *Inorg. Chem.* **1978**, *17*, 1008.

Contribution from the Departments of Chemistry, York University, Downsview, Toronto, Ontario, Canada M3J 1P3, and University of Washington, Seattle, Washington 95195

## Electronic Spectra of Phthalocyanine Radical Anions and Cations

P. C. MINOR,<sup>1a</sup> M. GOUTERMAN,<sup>\*1b</sup> and A. B. P. LEVER<sup>\*1a</sup>

Received May 9, 1984

The oxidation and reduction of metal phthalocyanines give rise to at least six oxidation states whose electronic spectra are rationalized in some depth in terms of SCF energies and Coulomb and exchange integrals. It is shown that a single set of parameters can reproduce the Q-band energies moderately well. Further, this same set of energies can reproduce differences in electrochemical potentials observed within this redox set. The pattern of variation in the Q-band energies (and in their number) now provides a means for identifying whether it is the metal or the phthalocyanine ligand that is reduced upon addition of an electron to the system.

### Introduction

During the past few years, there has been considerable resurgence in interest in the chemistry of the phthalocyanines (Pc). Their high thermal and chemical stability, coupled with their extensive redox chemistry, makes them excellent candidates for electrocatalytic and photocatalytic processes.<sup>2-5</sup>

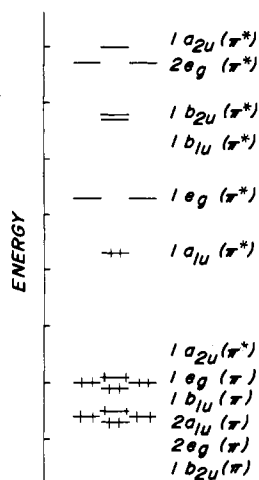
Our ultimate goal must be to possess sufficient understanding of the electronic structure of these molecules to be able to design catalysts to function in a specified fashion.

Recently our understanding of the electronic spectra of typical MPc complexes (containing the stable ligand oxidation state  $\text{Pc}^{2-}$ ) has been extended to include charge-transfer transitions.<sup>6</sup> We

(1) (a) York University. (b) University of Washington.  
(2) Zagal, J.; Sen, R. K.; Yeager, E. *J. Electroanal. Chem.* **1977**, *83*, 207.  
(3) Jahnke, H.; Schonborn, M.; Zimmerman, G. *Top. Curr. Chem.* **1976**, *61*, 13.

(4) Lever, A. B. P.; Licoccia, S.; Ramaswamy, B. S.; Kandil, A.; Stynes, D. V. *Inorg. Chim. Acta.* **1981**, *51*, 169.

(5) (a) Giraudeau, A.; Fan, F.-R.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 5137. (b) Green, J. M.; Faulkner, L. R. *J. Am. Chem. Soc.* **1983**, *2950*.



**Figure 1.** Energies of the highest occupied and lowest unoccupied molecular orbitals.<sup>8</sup> The molecular orbitals are numbered sequentially, up and down, from the Fermi level.

have also presented a detailed explanation of the redox characteristics of these systems as a function of metal ion, oxidation state, solvent, substituent, etc.<sup>7</sup>

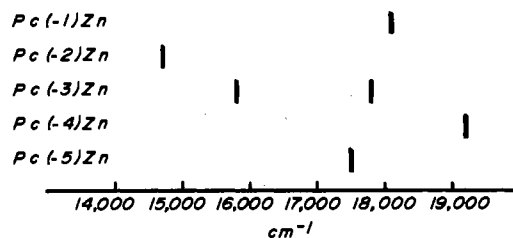
Photo- or electroredox cycles involving main-group MPCs will necessarily proceed via Pc anions or Pc cations. An analysis of the electronic spectra of such species should provide a clearer appreciation of how such systems might be involved in a catalytic process.

#### Initial Observations

The electronic structure of the  $Pc^{2-}M^n$  species can be understood through the work of Gouterman and co-workers.<sup>8-10</sup> Figure 1 illustrates the sequence and energies of the molecular orbitals lying near the HOMO and LUMO levels, which are of relevance to this spectroscopic study.

The two principal visible region features are the Q-band [ $1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$ ] near 600–750 nm with its associated vibrational satellites and the B- or Soret band [ $1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$ ] near 325–425 nm. Several intense ultraviolet region transitions include  $\pi \rightarrow \pi^*$  transitions from deeper lying  $\pi$  orbitals to  $1e_g(\pi^*)$ , e.g. the N band ( $1b_{1u}(\pi)$ ,  $2a_{2u}(\pi)$ ,  $1b_{2u}(\pi) \rightarrow 1e_g(\pi^*)$ ).<sup>10,11</sup> There is some evidence<sup>8-10</sup> that shoulders on the lower energy edge of the Soret may be transitions of the  $n \rightarrow \pi$  type from peripheral (bridging) azo links. These orbitals are located, energetically, near the HOMO level.<sup>10,11</sup> Except for those indicated above, no Pc-localized electronic spin-allowed transitions are expected energetically below the Soret. However, where empty metal d orbitals lie inside the HOMO–LUMO gap, LMCT transitions of the general type  $Pc(\pi) \rightarrow d$  may be anticipated. These can occur in the near-IR, below the Q-band, or between the Q and Soret absorption as has been extensively discussed.<sup>6,13</sup>

$Pc^{2-}M$  may be sequentially reduced up to four times by addition of electrons to the  $1e_g(\pi^*)$  LUMO level. One- or two-electron oxidation occurs by removal of electrons from the  $1a_{1u}$  HOMO. Clack and Yandle<sup>12</sup> have prepared many of the anionic species by chemical reduction and have reported their electronic spectra. Lever and Myers<sup>14</sup> and Hush and co-workers<sup>15</sup> reported a col-



**Figure 2.** Peak energies for the Q bands [ $1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$ ] for  $[Pc^x-Zn]^{(2-x)+}$  ( $x = 1-5$ ).

lection of cation radical  $Pc^+M^n$  data. This work represents the first systematic assignment and detailed interpretation of this body of data. Each oxidized or reduced species has a characteristic spectrum that may include low-energy absorption in the near-infrared, multiple-Q, or Soret regions and additional charge-transfer (CT) transitions.

Table I summarizes the relative energies of a range of main-group and transition-metal phthalocyanine radical anions and cations. Well-defined trends are clearly indicated in that most of the complexes behave in a parallel fashion. This is an important observation since it provides a means of identifying the various oxidized and reduced species. Since metal redox processes may reasonably be excluded on energetic grounds for main-group metals such as magnesium and closed subshell species such as zinc, the reduction of such species in four steps must yield  $Pc^{x-}M^{II}$  ( $x = 3-6$ ). Similarly, oxidation of the neutral species will yield  $Pc^{x-2}M^{II}Y_x$  where  $x = 1$  or 2 and Y is a counteranion.

Indeed, as illustrated graphically in Figure 2, the Q band varies as follows. Beginning with the cation radical  $Pc^+M$  (band usually near 18 000  $cm^{-1}$ ), reduction to  $Pc^{2-}M$  results in a more intense red-shifted Q band. Further reduction to  $Pc^{3-}M$  causes new absorption that is best interpreted in terms of the appearance of two new Q bands both blue shifted, and of lower intensity than  $Pc^{2-}M$ . Subsequent reduction to  $Pc^{4-}M$  results in a spectrum with a single broad Q band that is yet further blue shifted. Reduction to  $Pc^{5-}M$  now results in a red shift in the Q band. Finally, reduction to  $Pc^{6-}M$  causes the  $1e_g(\pi^*)$  level to be filled such that no Q bands are possible. However, a pair of new absorption bands some 4000  $cm^{-1}$  apart appear in the red end of the visible region and, as will be seen, are associated with the  $1e_g(\pi^*)$  level. All of the main-group complexes so far studied, and some of the transition-group complexes, behave in a manner exactly analogous to that described here. Such complexes are defined here as "well-behaved".

With transition-metal species such as  $[Pc^{2-}Fe^{II}]$ , redox can occur either at the metal or the ligand. From previous work<sup>16-18</sup> it is known that the first reduction in both  $Fe^{II}Pc$  and  $Co^{II}Pc$  occurs at the metal to yield  $[Pc^{2-}M^I]^-$ . Where the data parallel the main-group species, i.e. are well-behaved, subsequent reduction can be assumed to occur at the ring and not the metal. Any deviations from regular behavior should signal a change in oxidation state (or possibly spin state) at the metal. In general, ESR and magnetic data can also indicate whether redox has occurred at the metal or ring. Thus, for example in the cobalt Pc system, reduction of  $Pc^{2-}Co^{II}$  to  $Pc^{2-}Co^I$  occurs, followed by behavior paralleling that of zinc Pc described above; i.e., subsequent reduction occurs to the ring of the  $Co^I Pc$  system.

The transition-group phthalocyanines generally show some additional features that are likely to be charge transfer in origin.

#### Results and Discussion

As a starting point it is assumed that the one-electron energies of the various  $\pi$  and  $\pi^*$  orbitals do not vary very much from one oxidation level to another. This is a reasonable assumption based on the fact that an 18- $\pi$ -electron system is being considered, and

- (6) Lever, A. B. P.; Licoccia, S.; Minor, P. C.; Ramaswamy, B. S.; Pickens, S. R.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.
- (7) Lever, A. B. P.; Licoccia, S.; Magnell, K.; Minor, P. C.; Ramaswamy, B. S. *ACS Symp. Ser.* **1982**, *No. 201*, 237.
- (8) Gouterman, M.; Wagniere, G. H.; Snyder, L. C., Jr. *J. Mol. Spectrosc.* **1963**, *11*, 2.
- (9) Weiss, C.; Kobayashi, H.; Gouterman, M. *J. Mol. Spectrosc.* **1965**, *16*, 415.
- (10) McHugh, A. J.; Gouterman, M.; Weiss, J. *Theor. Chim. Acta* **1972**, *24*, 346.
- (11) Henriksson, A.; Sundbom, M. *Theor. Chim. Acta* **1972**, *27*, 213.
- (12) Clack, D. W.; Yandle, J. R. *Inorg. Chem.* **1972**, *11*, 1738.
- (13) Stillman, M. J.; Thompson, A. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *805*.
- (14) Myers, J. F.; Rayner-Canham, G. W.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461.

- (15) Hush, N. S., private communication, 1983.
- (16) Lever, A. B. P.; Wilshire, J. P. *Can. J. Chem.* **1976**, *54*, 2514.
- (17) Lever, A. B. P.; Wilshire, J. P. *Inorg. Chem.* **1978**, *17*, 1145.
- (18) Lever, A. B. P.; Minor, P. C. *Adv. Mol. Relax. Interact. Processes* **1980**, *18*, 115.

**Table I.** Electronic Spectra of Phthalocyanine Anions and Cations<sup>a</sup>

	Co <sup>III</sup> Pc <sup>-</sup>	Co <sup>III</sup> Pc <sup>2-</sup>	Co <sup>II</sup> Pc <sup>2-</sup>	Co <sup>I</sup> Pc <sup>2-</sup>	
$\pi-\pi(1)$	13 370				
Q	18 000	14 660	14 885	14 410 (0.23)	
$\pi-\pi(2)$	22 570				
CT				21 410 (0.76)	
Soret	28 550	27 170	28 735	32 050 (vs)	
N	35 640				
ref	14	35	36	12	
	Cr <sup>III</sup> Pc <sup>-</sup>	Cr <sup>III</sup> Pc <sup>2-</sup>	Zn <sup>II</sup> Pc <sup>-</sup>	Si <sup>IV</sup> Pc <sup>-</sup>	
$\pi-\pi(1)$	12 540		13 460	11 810	
Q	17 350	14 795	18 150	18 190	
$\pi-\pi(2)$	22 470		22 430	25 060	
CT					
Soret	27 590	29 070	26 360	34 920	
N	35 700	37 300	30 980?	39 980	
ref	14	36	14	15	
	Fe <sup>III</sup> Pc <sup>-</sup>	Fe <sup>III</sup> Pc <sup>2-</sup>	Fe <sup>II</sup> Pc <sup>2-</sup>	Fe <sup>I</sup> Pc <sup>2-</sup>	
$\pi-\pi(1)$	12 220				
Q	16 740	14 970	15 250	14 900	
$\pi-\pi(2)$	22 960				
CT				22 700	
Soret	27 030	30 700	30 350	30 700	
N	36 360				
ref	14	37	36	37	
	Mg <sup>II</sup> Pc <sup>2-</sup>	Ni <sup>II</sup> Pc <sup>2-</sup>	ClAlPc <sup>2-</sup>	Mn <sup>II</sup> Pc <sup>2-</sup>	Zn <sup>II</sup> Pc <sup>2-</sup>
Q	14 900	14 900	14 500	14 700	14 685
Soret	29 410	28 490	28 570		28 820
ref	36	36	36	36	36
	MgPc <sup>3-</sup>	MgPc <sup>4-</sup>	MgPc <sup>5-</sup>	MgPc <sup>6-</sup>	
$\pi^*-\pi^*(1)$	10 420 (0.01)	...	8970 (0.02)	11 910 (0.21)	
-V	11 630	11 110			
-V	12 530	12 500			
		16 260			
$\pi^*-\pi^*(2)$			12 120 (0.08)	16 130 (0.40)	
Q	15 670 (0.16)	19 230 (0.62)	16 950 (0.52)		
Q	17 790 (0.24)	...	...		
Soret	23 810 (0.20)	29 850 (0.69)	29 500 (0.88)		
Soret	29 410 (0.085)				
UV				24 270 (0.26)	
UV				32 790 (0.58)	
ref	12	12	12	12	
	ClAlPc <sup>3-</sup>	ClAlPc <sup>4-</sup>	ClAlPc <sup>5-</sup>	ClAlPc <sup>6-</sup>	
$\pi^*-\pi^*(1)$	10 260 (0.03)		9620 (0.03)	12 350 (0.09)	
-V	11 110	11 110			
-V	12 200	12 500			
	13 810				
$\pi^*-\pi^*(2)$			13 330	16 560 (0.16)	
Q	16 180 (0.07)	19 310 (0.27)	17 040 (0.20)		
Q	17 390 (0.12)				
Soret	30 400 (0.54)	30 580 (0.49)	30 120 (0.42)		
Soret	...				
UV				28 990 (0.39)	
ref	12	12	12	12	

<sup>a</sup>Numbers in parentheses are oscillator strengths; s = strong, vs = very strong. For data for reduced iron species, see ref 12. <sup>b</sup>Probably contained within Q band. For solvents and conditions, please see the original literature.

therefore loss or gain of one or two electrons has little effect upon bond order. Moreover, the molecular geometry is fairly rigid. Note the similarity, for example, between the X-ray structural characteristics of ZnTPP and its radical cation ZnTPP<sup>+</sup>.<sup>19</sup>

Thus, in a cation radical, changes in spectra will reflect the existence of a "hole" in  $1a_{1u}$  (and hence additional transitions of the type  $e_g(\pi)-1a_{1u}(\pi)$  are expected) and changes in spin-pairing energy. In addition, a small change in geometry may be anticipated for anion radicals. Thus, the monoanion radical  $Pc^{3-}M$  will possess a  ${}^2E_g$  ground term that is subject to Jahn-Teller distortion. Although the degree of distortion cannot be very large because of the stereochemical rigidity of the molecule, it is suf-

	ZnPc <sup>3-</sup>	ZnPc <sup>4-</sup>	ZnPc <sup>5-</sup>	ZnPc <sup>6-</sup>
$\pi^*-\pi^*(1)$	10 550 (0.07)		9090 (0.15)	12 180 (vs)
-V	11 770	12 950		
-V	12 740			
$\pi^*-\pi^*(2)$				16 130 (vs)
Q	15 720 (s)	19 160 (vs)	17 540 (vs)	
Q	17 790 (s)	...	...	
Soret	30 960 (vs)	29 850 (vs)	29 410 (vs)	
Soret				
UV				32 890 (vs)
ref	12	12	12	12
	NiPc <sup>3-</sup>	NiPc <sup>4-</sup>	NiPc <sup>5-</sup>	NiPc <sup>6-</sup>
$\pi^*-\pi^*(1)$	10 930 (0.02)	10 990	9220 (0.13)	11 360 (0.93)
-V	11 830	11 360	11 240	
-V	12 350	11 770		
$\pi^*-\pi^*(2)$				14 880 (s)
Q	15 870 (0.45)	18 660 (s)	16 950 (vs)	
Q	17 610 (0.72)			
Soret	30 030 (vs)	30 030 (vs)	30 000 (vs)	
Soret				
UV				32 150 (vs)
ref	12	12	12	12
	Co <sup>I</sup> Pc <sup>3-</sup>	Co <sup>I</sup> Pc <sup>4-</sup>	Co <sup>I</sup> Pc <sup>5-</sup>	Co <sup>I</sup> Pc <sup>6-</sup>
$\pi^*-\pi^*(1)$	10 870 (0.05)	8480 (0.06)	10 000	11 300 (0.06)
-V		11 050 (0.08)	11 490 (0.1)	
-V				
$\pi^*-\pi^*(2)$				14 490 (0.4)
Q	14 680 (0.18)	19 610 (vs)	17 480 (1.06)	
Q	16 000 (0.14)			
CT	21 010 (s)	<i>b</i>	23 700 (0.52)	18 520 (0.94)
Soret	31 350 (vs)	30 670 (s)	?	
ref	12	12	12	12
	MnPc <sup>3-</sup>	MnPc <sup>4-</sup>	MnPc <sup>5-</sup>	MnPc <sup>6-</sup>
$\pi^*-\pi^*(1)$				12 020 (vs)
-V				
-V	very rich complex spectrum			
$\pi^*-\pi^*(2)$				16 130 (vs)
CT		14 120 (0.43)	9090 (0.5)	
Q		19 160 (vs)	17 670 (vs)	
Q				
Soret		30 210 (s)	29 410 (s)	
Soret				
UV				27 030 (s)
ref	12	12	12	12

ficiently large to cause spin pairing in the dianion radicals  $Pc^{4-}M$ , which, for main-group metals, are known to be diamagnetic,<sup>12,20</sup> as discussed below.

Our concern is to understand the regular shift in Q band indicated in Figure 2, assign all the bands in the spectra of the various species (Table I), derive some fundamental energy information from the spectroscopic changes, and indicate a relationship between spectroscopically and electrochemically defined energy parameters. In particular, our discussion represents a simplification of earlier work by Hush<sup>21</sup> and by Linder et al.<sup>22</sup>

(19) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 982.

(20) Lexa, D.; Reix, M. *J. Chem. Phys. Physiol. Biol.* **1974**, *71*, 517. Taube, R. Z. *Chem.* **1966**, *6*, 8. Rollman, L. D.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1485. Gloss, G.; Gloss, L. *J. Am. Chem. Soc.* **1963**, *85*, 818.

that we hope will be more useful for the experimentalist; also, we will discuss more explicitly the role of the Jahn–Teller effects in these systems.

Except where indicated below, the literature assignments of ring oxidation or reduction are accepted. On these bases, the spectroscopic data may be interpreted. First, a qualitative discussion is presented for comparison with the experimental data and then, later, a semiquantitative analysis attempted.

(i) **Cation Radical  $\text{Pc}^{\cdot+}\text{M}^n$ .** The ground-state configuration,  $(a_{2u})^2a_{1u}$ , gives a  ${}^2A_{1u}$  state. The following consequences may be predicted, relative to the unoxidized  $\text{Pc}^2-\text{M}$  species: (a) The Q band shifts to high energy due to differential spin-pairing energy, as discussed below. (b) The Soret and N band should be little affected compared with the  $\text{Pc}^2-\text{M}$  species. (c) The presence of a hole in  $1a_{1u}$  permits allowed transitions from  $e_g(\pi)$  levels lying below the  $1a_{1u}$ .

Indeed, bands attributable to the Q, Soret, and N bands are readily identified in the spectra of the cation radicals, as shown in Table I. From its energy and intensity the band near 12 000  $\text{cm}^{-1}$  is reasonably associated with  ${}^2E_g \leftarrow {}^2A_{1u} (1e_g(\pi) \rightarrow 1a_{1u}(\pi))$  as proposed. There is, however, an additional strong feature lying between the Q and Soret bands. This cannot arise via excitation from  $\pi-\pi^*$  nor from a charge-transfer transition or it would also be observed in the unoxidized species. Thus, it must be associated with the hole in  $1a_{1u}$ . At lower energies there is a second orbital  $2e_g(\pi)$  (Figure 1), and transition therefrom to  $1a_{1u}$  seems a proper assignment for this extra feature. Some care must be exercised in interpreting solid-state spectra since broadening and extra peaks may arise through intermolecular coupling (Davydov splitting). However, the agreement between predicted and observed spectra is good, and the assignments are probably correct.

(ii) **Monoanion  $\text{Pc}^{\cdot-}\text{M}^n$ .** The ground electron configuration,  $(a_{1u})^2e_g$ , produces a degenerate term  ${}^2E_g$ . The following consequences are expected: (a) Again, the Q band shifts to higher energy due to a difference in spin-pairing energy, as discussed below. (b) The ground state,  ${}^2E_g$ , is subject to a JT distortion. However, this is not expected to be large enough to dominate the spectroscopic effects, since the JT effect of the configuration  $(a_{1u})^2e_g$  of the monoanion should be comparable to that of the Q band of the neutral,  $a_{1u}e_g$ . For the latter, the small Stokes shift between absorption and fluorescence shows that the JT effect is small. (c) The Q band arises from the configuration  $a_{1u}(e_g)^2$ , which gives rise to states  ${}^4A_{2u}$ ,  ${}^2A_{1u}$ ,  ${}^2A_{2u}$ ,  ${}^2B_{1u}$ , and  ${}^2B_{2u}$ . Electron-exchange terms are expected to lift the degeneracy of the four doublet states, thus explaining the presence of two bands in the Q region, 1200–2200  $\text{cm}^{-1}$  apart, as discussed below. (d) Allowed far-red bands arise from the  $\pi^*-\pi^*$  transitions  $1e_g(\pi^*) \rightarrow 1b_{nu}(\pi^*)$  ( $n = 1, 2$ ) where  $1b_{1u}(\pi^*)$  and  $1b_{2u}(\pi^*)$  are higher energy  $\pi^*$  MO's of the neutral (Figure 1). These  ${}^2B_{1u}$  and  ${}^2B_{2u}$  excited states have symmetries similar to two of the four  ${}^2Q$  states mentioned above. (e) There will be four Soret excited states with the same symmetries as the  ${}^2Q$  states. Thus, two of the  ${}^2Q$  states will be subject to configuration interaction (CI) as in the neutral, and two will experience CI from states to both lower and higher energies; these latter may not then be moved by CI. The well-resolved far-red band at 10 400–11 000  $\text{cm}^{-1}$  with which the spectrum begins shows satellites 1000 and 2000  $\text{cm}^{-1}$  to the blue, which are probably vibronic overtones.

(iii) **Dianion  $\text{Pc}^{2-}\text{M}^n$ .** As an open shell, the ground-state  $(a_{1u})^2(e_g)^2$  would be expected to be a triplet. However, experimental studies<sup>22</sup> show it is a singlet. As discussed below, this can be explained by a pseudo JT effect that stabilizes  ${}^1B_{1g}$  with respect to  ${}^3A_{2g}$ . The following spectroscopic effects may be expected: (a) The Q states, arising from the configuration  $a_{1u}(e_g)^3$ , have symmetry  ${}^2E_u$ , which are subject to a JT effect as in the neutral. This combined with the pseudo JT effect in the  ${}^1B_{1g}$  ground state should lead to a broadened absorption, as is observed. A Soret band is expected and is observed at 30 000  $\text{cm}^{-1}$ . (b) Additional transitions,  $\pi^*-\pi^*$ , as in the monoanion are expected. However, unlike the

monoanion, the absorption in the near-infrared does not begin with a sharp band followed by a weaker vibronic. Rather, it begins with a progression of two or three vibronics of comparable intensity.<sup>12</sup> This difference from the monoanion we ascribe to the pseudo JT distorted ground state combined with the JT distorted excited configuration  $(a_{1u})^2e_gb_{1u}$ .

(iv) **Trianion  $\text{Pc}^{3-}\text{M}^n$ .** The ground configuration,  $(a_{1u})^2(e_g)^3$ , gives rise to a  ${}^2E_g$  state, which should have a small JT distortion as in the monoanion. (a) The Q band arising from the configuration  $a_{1u}(e_g)^4$  and the Soret band arising from  $a_{2u}(e_g)^4$  have excited states  ${}^2A_{1u}$  and  ${}^2A_{2u}$ , respectively, which are not subject to mutual configuration interaction. (b) The  $\pi^*-\pi^*$  excited states have configurations  $(e_g)^2b_{1u}$  or  $(e_g)^2b_{2u}$ . These give rise to two transitions to the red of the Q bands in  $\text{Pc}^{3-}\text{Mg}^{11}$  at 9000 and 12 000  $\text{cm}^{-1}$ . These states can have configuration interaction with the Q excited states, since they produce terms  ${}^2A_{1u}$ ,  ${}^2A_{2u}$ ,  ${}^2B_{1u}$ , and  ${}^2B_{2u}$ .

(v) **Tetraanion  $\text{Pc}^{4-}\text{M}^n$ .** The  $e_g$  orbitals are now filled and the ground state is  ${}^1A_{1g}$ . (a) No Q or Soret bands are seen nor are expected. (b) Excited states observed at  $\sim 12 000$  and  $\sim 16 000$   $\text{cm}^{-1}$  can be attributed to  $\pi^*-\pi^*$  transitions,  $e_g(\pi^*) \rightarrow b_{1u}(\pi^*)$ ,  $b_{2u}(\pi^*)$ . These are significantly to the blue of the  $\pi^*-\pi^*$  transition of the less reduced anions. Linder et al.,<sup>22</sup> who did detailed calculations on the anions, showed that use of neutral phthalocyanine orbitals can give a poor fit to the energies and that SCF orbitals of the tetraanion must be used.

It is clear that the overall features of all the spectra agree in general with expectation. However, certain questions are immediately apparent. What are the assignments of additional bands seen in some of the transition-metal phthalocyanine species? Are the absolute energies observed consistent with changes in spin-pairing energy, Jahn–Teller splitting, changes in configurational interaction, etc., and can any of these quantities be derived? Are there relationships between the electrochemical potentials for oxidation and reduction and the observed transition energies?

(i) **Transition-Metal Phthalocyanine CT Spectra.** Consider first the series of cobalt complexes  $[\text{Pc}^2-\text{Co}^{\text{III}}]^{2+}$ ,  $[\text{Pc}^2-\text{Co}^{\text{II}}]^{+}$ ,  $[\text{Pc}^2-\text{Co}^{\text{I}}]$ ,  $[\text{Pc}^{2-}\text{Co}^{\text{I}}]^{-}$ ,  $[\text{Pc}^{3-}\text{Co}^{\text{I}}]^{2-}$  ...  $[\text{Pc}^{6-}\text{Co}^{\text{I}}]^{5-}$  (where any axial ligands are omitted for clarity). This series behaves very much like a main-group phthalocyanine once reduction to the  $\text{Pc}^2-\text{Co}^{\text{I}}$  level is achieved, leading to the conclusion that the cobalt remains in the Co(I) state as reduction occurs at the ring.

An additional intense absorption occurs at 20 000–25 000  $\text{cm}^{-1}$  in all the reduced species containing Co(I). A previous MCD study<sup>13</sup> of  $[\text{Pc}^{2-}\text{Co}^{\text{I}}]$  assigned this to a Co(I) to Pc MLCT transition. Since an A term was observed in the MCD spectrum, the excited state must be doubly degenerate; the probable assignment is  $d(xz, yz) \rightarrow 1b_{1u}\pi^*$ . From the electrochemical procedure for identifying charge-transfer energies,<sup>6</sup> this transition is indeed predicted to lie in the region where this band is observed. The lack of any significant variation in the energy of this transition as the phthalocyanine is further reduced does imply that the  $1e_g(\pi^*)$  level to which electrons are being added is not involved, at least in first order, in this transition.

In the case of the species  $[\text{Co}^{\text{I}}\text{Pc}^{4-}]^{3-}$ , the Q and CT bands overlap to yield a very strong feature near 20 000  $\text{cm}^{-1}$ .

The species  $[\text{Pc}^2-\text{Fe}^{\text{III}}]^{2+}$ ,  $[\text{Pc}^2-\text{Fe}^{\text{II}}]^{+}$ ,  $[\text{Pc}^2-\text{Fe}^{\text{I}}]$ , and  $[\text{Pc}^{2-}\text{Fe}^{\text{I}}]^{-}$  have spectra as anticipated. The species  $[\text{Pc}^{2-}\text{Fe}^{\text{I}}]^{-}$ <sup>16,17</sup> has an extra strong band near 20 000  $\text{cm}^{-1}$  reasonably assigned as charge transfer from Fe(I) to  $\text{Pc}^{2-}$  (probably  $d(xz, yz) \rightarrow 1b_{1u}(\pi^*)$ ) (MLCT), but the Q band appears unusually weak. However, it is rather broad, and the total integrated intensity may not have diminished a great deal. Indeed, the peak molar intensity of the Q band does depend upon the oxidation state of the central metal ion, increasing and becoming narrower with increasing oxidation state.<sup>13</sup> The species formally at oxidation level  $\text{Pc}^3-\text{Fe}^{\text{I}}$  does not exhibit a doubling of the Q band but does show a strong additional band near 20 000  $\text{cm}^{-1}$ , suggesting it is an Fe(I) species. This is in agreement with earlier studies. The species formally  $\text{Pc}^4-\text{Fe}^{\text{I}}$  does possess a normal spectrum, but the charge-transfer band is now missing. The  $\text{Pc}^5-\text{Fe}^{\text{I}}$  species is again atypical. Clearly, the system requires further study for proper understanding, and this is in hand.<sup>23</sup>

(21) Hush, N. S. *Theor. Chim. Acta* 1966, 4, 108.

(22) Linder, R. E.; Rowlands, J. R.; Hush, N. S. *Mol. Phys.* 1971, 21, 417.

The first reduced manganese species is known<sup>24</sup> to be  $[\text{Pc}^{3-}\text{Mn}^{\text{II}}]^-$  whose spectrum is very rich. While the doubled Q band may be identifiable, there are a significant number of additional strong features that are presumably charge transfer in origin.<sup>6</sup> Triplet transitions, though expected to be fairly weak, may well contribute to the complexity of the spectrum. A clear assignment of this species is not yet possible.

However, the double and triply reduced species have spectra that parallel the data for the main-group analogues, but with one additional charge-transfer band (LMCT). It is likely, therefore, that they are  $\text{Pc}^4-\text{Mn}^{\text{II}}$  and  $\text{Pc}^{5-}\text{Mn}^{\text{II}}$ , i.e. reduction occurs at the ring. ESR data support this conclusion,<sup>25,26</sup> though with some ambiguity concerning  $\text{Pc}^4-\text{Mn}^{\text{II}}$ . The species  $\text{Pc}^6-\text{Mn}^{\text{II}}$  has the usual doublet  $\pi^*-\pi^*$  transitions, but the CT band is curiously absent. Possibly it has shifted to very low energy (out of range of this study) since the Pc unit is now very readily oxidizable.

The spectra for the nickel(II) Pc species exactly parallel the main-group data since no change in oxidation state of the nickel ion is expected<sup>18</sup> and no charge transfer is expected in the region under study.<sup>6</sup>

In summary, the main-group complexes, nickel and cobalt species, all have parallel well-behaved deportment. The lower oxidation states of the manganese species are also well-behaved, but there are evidently some subtle changes in redox behavior for the iron series.

**(ii) Semiquantitative Approach.** There are four factors that need to be considered in discussion of the spectra of the anions. Listed in what we consider their order of importance, these are: (1) the one-electron energy difference between the orbitals of the transitions; (2) the two-electron Coulomb and exchange integrals, i.e. the change in repulsion energy due to the transition; (3) the Jahn-Teller and pseudo Jahn-Teller effects; (4) configuration interaction among the various states.

Linder et al.<sup>22</sup> did a quite careful treatment of ground and excited states of the mono-, tri-, and tetraanions. Our goal is to present a simpler treatment that we hope will be more accessible to the experimentalist yet still useful for understanding the observed spectroscopic generalities. We shall start with the one-electron Hartree-Fock operator for the neutral ground state.

$$F = H^{\text{core}} + \sum_j (2J_j - K_j) \quad (1)$$

Here,  $H^{\text{core}}$  is the one-electron operator for electron kinetic energy and its Coulomb potential energy interaction with the nuclei and any electrons in a frozen core; the  $J_j$  and  $K_j$  are Coulomb and exchange operators that depend on the doubly occupied orbital  $\Phi_j$  of the neutral ground state as defined by Roothaan.<sup>27</sup> For molecular orbitals we have

$$F\Phi_k = \epsilon_k \Phi_k \quad (2)$$

where  $\Phi_k$  are the SCF orbitals and  $\epsilon_k$  are the SCF energies of the neutral ground state. For any orbital  $\Phi_i$  we have

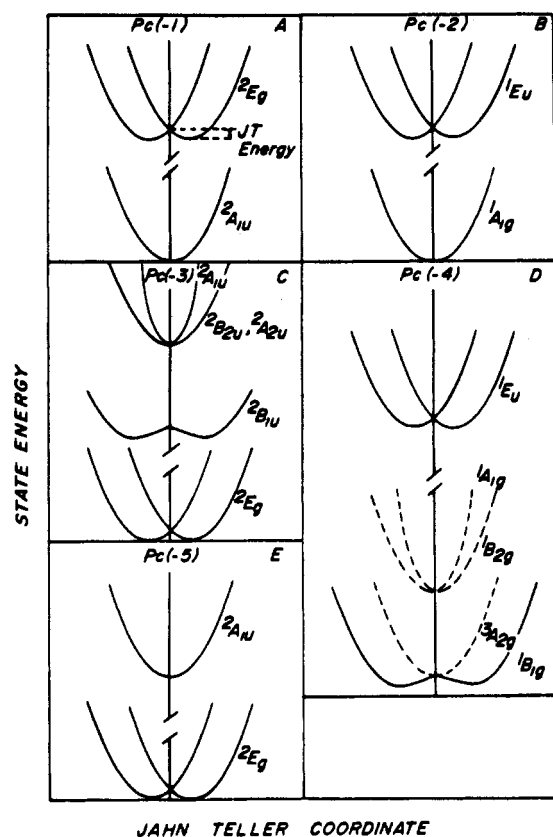
$$\langle \Phi_i | J_j | \Phi_i \rangle = J_{ij} \quad \langle \Phi_i | K_j | \Phi_i \rangle = K_{ij} \quad (3)$$

Here,  $J_{ij}$  and  $K_{ij}$  are Coulomb and exchange integrals with their usual definition.<sup>28</sup> In Table II we list the energies for transitions from the ground to the Q state, i.e. the transition  $1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$ , in terms of  $\epsilon_i$  and the various  $J_{ij}$  and  $K_{ij}$ . In doing this, the orbital energies are assumed to remain invariant as in the neutral and we calculate the energies at the  $D_{4h}$  equilibrium position. In Table III we have listed the energy for reduction of each species in this same approximation. Tables II and III then

**Table II.** Transition Energies and Transition Moments for Q States of Phthalocyanine Species

species	transition	energy <sup>a,b</sup>	transition moment <sup>c</sup>
$\text{Pc}^-$	${}^2E_g \rightarrow {}^2A_{1u}$	$\Delta E + J_{aa} - J_{ax} + K_{ax} = 18.8^d$	$R^2$
$\text{Pc}^{2-}$	${}^3E_1 \rightarrow {}^1A_{1g}$	$\Delta E = 12.3^f (9.1-10.6)^e$	0
	${}^1E_u \rightarrow {}^1A_{1g}$	$\Delta E + 2K_{ax} = 14.5^d$	$4R^2$
$\text{Pc}^{3-}$	${}^2B_{1u} \rightarrow {}^2E_g$	$\Delta E + J_{xx} - J_{ax} + K_{ax} - K_{xy} = 15.5^d$	$R^2/2$
	${}^2B_{2u} \rightarrow {}^2E_g$	$\Delta E + J_{xy} - J_{ax} + K_{ax} + K_{xy} = 17.7^d$	$R^2/2$
	${}^2A_{2u} \rightarrow {}^2E_g$	$\Delta E + J_{xy} - J_{ax} + 3K_{ax} - K_{xy} = 15.5^d$	$3R^2/2$
	${}^2A_{1u} \rightarrow {}^2E_g$	$\Delta E + J_{xx} - J_{ax} + K_{ax} + K_{xy} = 17.7^d$	$R^2/2$
$\text{Pc}^{4-}$	${}^1E_u \rightarrow {}^1B_{1g}$	$\Delta E + J_{xy} + J_{yy} - 2J_{ax} + 3K_{ax} = 22.0^f (19.0)^g$	$2R^2$
$\text{Pc}^{5-}$	${}^2A_{1u} \rightarrow {}^2E_g$	$\Delta E + 2J_{xy} + J_{xx} - 3J_{ax} + 2K_{ax} - K_{xy} = 23.0^f (17.3)^g$	$R^2$

<sup>a</sup> Abbreviations:  $a = a_{1u}$ ,  $x = e_{gx}(\pi^*)$ ,  $y = e_{gy}(\pi^*)$ .  $D_{4h}$  symmetry is assumed, thereby fixing  $\epsilon_x = \epsilon_y$ ,  $J_{xx} = J_{yy}$ ,  $J_{ax} = J_{ay}$ , and  $K_x = K_y$ . <sup>b</sup>  $\Delta E = \epsilon_x - \epsilon_a - J_{ax}$ . <sup>c</sup>  $R = \langle a_{1u}(\pi) | x | e_{gx} \rangle$ . <sup>d</sup> These numbers are rough averages of the data for these transitions for the main-group phthalocyanines and are fitted assuming  $J_{xx} = J_{xy}$ ,  $K_{ax} = K_{ay}$ ,  $\Delta E = 12300$ ,  $J_{aa} - J_{ax} = 5400$ ,  $J_{xx} - J_{ax} = 3200$ , and  $K_{xy} = 1100 \text{ cm}^{-1}$ . <sup>e</sup> Experimental data.<sup>31</sup> <sup>f</sup> Calculated using the values in (d). <sup>g</sup> Experimental numbers from Figure 2.



**Figure 3.** Potential energy curves showing schematically the effect of a Jahn-Teller mode on the excited states of phthalocyanine species: A monocation; B, neutral; C, monoanion; D, dianion; E, trianion. The arrow, in panel A, shows the definition of the JT energy.

represent a simple treatment of the factors (1) and (2), the orbital energy differences, and the differences among Coulomb and exchange integrals.

Table II also contains an estimate of the relative oscillator strengths of the various redox species normalized to the oscillator strength of the neutral 2- species. In fact, agreement with experiment is rather poor—however, it is extremely difficult to obtain accurate intensity data for the reduced species; thus, the literature values probably contain significant experimental error. Moreover, the simple molecular orbital analysis<sup>28</sup> used to obtain the relative oscillator strengths is not expected to be highly accurate.

Several features can be seen in Tables II and III. Note that for the cation and the neutral, the transition is from a simple

- (23) Hempstead, M.; Minor, P. C.; Lever, A. B. P., work in progress.  
 (24) Lever, A. B. P.; Minor, P. C.; Wilshire, J. P. *Inorg. Chem.* **1980**, *20*, 2550.  
 (25) Cookson, D. J.; Smith, T. D.; Boas, J. F.; Hicks, P. R.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **1977**, 211.  
 (26) Livorness, J.; Smith, T. D.; Pilbrow, J. R.; Sinclair, G. R. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 425-426.  
 (27) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.  
 (28) (a) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962; Chapter 2. (b) Lever, A. B. P. "Inorganic Electronic Spectroscopy", 2nd ed.; Elsevier: Amsterdam, 1984.

**Table III.** Optical and Electrochemical Energies for Reduction of Phthalocyanine Species

redn step	states	$\Delta w$	$-FE^0 - C$	$\Delta(-FE^0)^b$	$\Delta(-FE^0)^c$
Pc <sup>-</sup> -Pc <sup>2-</sup>	<sup>2</sup> A <sub>1u</sub> - <sup>1</sup> A <sub>1g</sub>	$\epsilon_a$	$\Delta w - \alpha$	$\epsilon_x - \epsilon_a + 2\alpha = 13,300$	$\epsilon_c - \epsilon_a - J_{ax} + 2K_{ax} = 14,500$
Pc <sup>2-</sup> -Pc <sup>3-</sup>	<sup>1</sup> A <sub>1g</sub> - <sup>2</sup> E <sub>g</sub>	$\epsilon_x$	$\Delta w + \alpha$	$J_{xx} - K_{xy} + 2\alpha = 3200$	$J_{xx} - K_{xy} - J_{ax} + 2K_{ax} = 4300$
Pc <sup>3-</sup> -Pc <sup>4-</sup>	<sup>2</sup> E <sub>g</sub> - <sup>3</sup> A <sub>2g</sub> <sup>2</sup> E <sub>g</sub> - <sup>1</sup> B <sub>1g</sub> <sup>2</sup> E <sub>g</sub> - <sup>1</sup> B <sub>2g</sub> <sup>2</sup> E <sub>g</sub> - <sup>1</sup> A <sub>1g</sub>	$\epsilon_x + J_{xy} - K_{xy}$ $\epsilon_x + J_{xx} - K_{xy}$ $\epsilon_x + J_{xy} + K_{xy}$ $\epsilon_x + J_{xx} + K_{xy}$	$\Delta w + 3\alpha$	$2J_{xy} - J_{xx} + K_{xy} + 2\alpha = 4800$	$2J_{xy} - J_{xx} + K_{xy} - J_{ax} + 2K_{ax} = 6500$
Pc <sup>4-</sup> -Pc <sup>5-</sup>	<sup>1</sup> B <sub>1g</sub> - <sup>2</sup> E <sub>g</sub>	$\epsilon_x + 2J_{xy}$	$\Delta w + 5\alpha$	$J_{xx} - K_{xy} + 2\alpha = 3200$	$J_{xx} - K_{xy} - J_{ax} + 2K_{ax} = 4300$
Pc <sup>5-</sup> -Pc <sup>6-</sup>	<sup>2</sup> E <sub>g</sub> - <sup>1</sup> A <sub>1g</sub>	$\epsilon_x + 2J_{xy} + J_{xx} - K_{xy}$	$\Delta w + 7\alpha$		

<sup>a</sup>C depends upon the reference electrode but cancels from the analysis. We assume with Hush<sup>21</sup> that the free energy for ion solvation is  $n^2\alpha$ , where  $n$  is the species charge and  $\alpha$  is a negative multiplier. <sup>b</sup>This column is the difference between the entries in column 4 above and below it. The numbers (wavenumbers) are experimental average energies from electrochemical data.<sup>7</sup> <sup>c</sup>The expressions in this column arise from column 5 replacing  $2\alpha$  by  $-J_{ax} + 2K_{ax}$ . The numbers are the solutions for these expressions using the optical data analysis in the text and the parameter values in Table II.

nondegenerate ground state to a degenerate excited state. This degeneracy implies a Jahn-Teller effect. The mode of operation of the JT effect is shown in Figure 3. For Pc<sup>-</sup> and Pc<sup>2-</sup> the effect is simply to shift the minimum of the excited state with respect to the ground state. The result would be to introduce a Franck-Condon progression in the Jahn-Teller mode.<sup>29</sup> The excited-state and ground-state potentials would then be described by the oscillator equations

$$H = \hbar\omega[(p^2 + q^2) + \lambda q] \quad (4)$$

where  $\lambda = 0$  in the ground state but  $\lambda \neq 0$  in the excited state. The JT energy defined in Figure 3A is just  $(\lambda^2/2)\hbar\omega$ . It can be shown<sup>30</sup> that the ratio

$$I(n,0)/I(0,0) = (\lambda^2/2)^n/n! \quad (5)$$

where  $I(n,0)$  is the intensity of the transition to the  $n$ th level in the JT mode and  $I(0,0)$  is the intensity of the origin. In particular  $I(1,0)/I(0,0) = \lambda^2/2 = (\text{JT energy})/(\text{vibrnl quantum}) < 0.2$  (6)

The estimate 0.2 comes from standard spectra for Pc<sup>2-</sup>.

The JT effect arises because of one extra electron in an  $e_{gx}(\pi^*)$  orbital, and is expected to be comparable for the monocation <sup>2</sup>E<sub>g</sub> excited state, the neutral <sup>1</sup>E<sub>u</sub> excited state, the monoanion <sup>2</sup>E<sub>g</sub> ground state, the dianion <sup>1</sup>E<sub>u</sub> excited state, and the trianion <sup>2</sup>E<sub>g</sub> ground state. This is illustrated schematically in Figure 3. The largest JT effect would naively be expected for configurations  $[e_g(\pi^*)]^2$ , which occur in the monoanion excited state and the dianion ground state. Here, the states  $(e_{gx})^2$  have twice the JT stabilization as  $(e_{gx})^1$  or  $(e_{gx})^2e_{gy}$ ; the states  $e_{gx}e_{gy}$  would have no JT effect. However, the states  $(e_{gx})^2$  and  $(e_{gy})^2$  are subject to configuration interaction, and the JT effect becomes second order or a "pseudo Jahn-Teller" effect.<sup>30</sup> This result is again illustrated in Figure 3 for the monoanion excited state, <sup>2</sup>B<sub>1u</sub>, and the dianion ground state, <sup>1</sup>B<sub>1g</sub>. The doubling of the monoanion Q band is attributed to the exchange energy splitting of the four doublet states that arise from the configuration  $a_{1u}(e_g)^2$ ; the Jahn-Teller effect contributes some vibronic broadening. For the dianion ground state the pseudo JT effect is very important, as it may be partly responsible for the fact that the ground state is <sup>1</sup>B<sub>1g</sub> rather than <sup>3</sup>A<sub>2g</sub>, as shown in Figure 3D. We attribute the great broadness observed in the dianion Q bands to the combination of the pseudo JT effect in the ground state and the JT effect in the excited state.

It would be useful to calculate the transition energies for the observed Q bands to rationalize the experimental data and also to relate these to the electrochemical data. Expressions for the Q-band excited-state energies are shown in Table II in terms of the SCF energies of  $1a_{1u}$  and  $1e_g$  defined as  $\epsilon_a$  and  $\epsilon_x$ , respectively,

**Table IV.** State Symmetries in Phthalocyanine Species<sup>a</sup>

state	Pc <sup>-</sup>	Pc <sup>2-</sup>	Pc <sup>3-</sup>	Pc <sup>4-</sup>	Pc <sup>5-</sup>	Pc <sup>6-</sup>
ground	<sup>2</sup> A <sub>1u</sub>	<sup>1</sup> A <sub>1g</sub>	<sup>2</sup> E <sub>g</sub>	<sup>1</sup> B <sub>1g</sub>	<sup>2</sup> E <sub>g</sub>	<sup>1</sup> A <sub>1g</sub>
Q level	<sup>2</sup> E <sub>g</sub>	<sup>1</sup> E <sub>u</sub>	<sup>2</sup> A <sub>1u</sub> , <sup>2</sup> A <sub>2u</sub>	<sup>1</sup> E <sub>u</sub>	<sup>2</sup> A <sub>1u</sub>	
Soret	<sup>2</sup> E <sub>g</sub>	<sup>1</sup> E <sub>u</sub>	<sup>2</sup> A <sub>1u</sub> , <sup>2</sup> A <sub>2u</sub>	<sup>1</sup> E <sub>u</sub>	<sup>2</sup> A <sub>2u</sub>	
$\pi^*-\pi^*$			<sup>2</sup> B <sub>1u</sub> , <sup>2</sup> B <sub>2u</sub>	<sup>1</sup> E <sub>u</sub>	<sup>2</sup> A <sub>1u</sub> , <sup>2</sup> A <sub>2u</sub>	<sup>1</sup> E <sub>u</sub>
$\pi-\pi$	<sup>2</sup> E <sub>g</sub>				<sup>2</sup> B <sub>1u</sub> , <sup>2</sup> B <sub>2u</sub>	

<sup>a</sup>Q and Soret bands as usually defined.  $\pi^*-\pi^*$  is transition from  $1e_g(\pi^*)$  into  $1b_{1u}(\pi^*)$  or  $1b_{2u}(\pi^*)$ .  $\pi-\pi$  is transition from  $1e_g(\pi)$  to  $1a_{1u}$ .

and the necessary Coulomb and exchange integrals, specifically  $J_{aa}$ ,  $J_{xx}$ ,  $J_{xy}$ ,  $K_{ax}$ , and  $K_{xy}$ , a total of seven variables in all. We follow Hush<sup>21</sup> and assume  $J_{xx} = J_{xy}$  to account for the singlet ground state of the dianion. Moreover, we assume  $K_{ax} = K_{xy}$ . By analysis of the expressions for the Q-band transition energies, it is possible to group the variables into four parameters as shown in Table II, namely

$$\Delta E = \epsilon_x - \epsilon_a - J_{ax} \quad J_{aa} - J_{ax} \quad J_{xx} - J_{ax} \quad K_{xy} \quad (7)$$

These have been fitted to the average Q-band energies displayed by the Pc<sup>-</sup>, Pc<sup>2-</sup>, and Pc<sup>3-</sup> species. As shown in Table II, the best fit is obtained with

$$\Delta E = 12,300 \quad J_{aa} - J_{ax} = 5400 \quad J_{xx} - J_{ax} = 3200 \quad K_{xy} = 1100 \text{ cm}^{-1} \quad (8)$$

which reproduce the behavior of these three oxidation states moderately well. The absorption energies of the Pc<sup>4-</sup> and Pc<sup>5-</sup> species, as well as the triplet transition of the Pc<sup>2-</sup> species,<sup>31</sup> have also been calculated. Although the fit to these latter species is not so favorable, they are qualitatively correct in showing that the dianion and trianion, like the cation, are blue shifted with respect to the neutral species (Table II).

What factors enter a more exact treatment? We have conceptually extended the SCF energies from the neutral to the other species. Linder et al.<sup>22</sup> showed that calculations on the tetraanion  $\pi^*-\pi^*$  transitions totally failed when orbitals of the neutral were used, and for a good fit it was necessary to use the SCF orbitals of the tetraanion itself. It is reasonable to expect that in the higher anions the energy gap between  $a_{1u}(\pi)$  and  $e_g(\pi^*)$  might decrease [i.e.,  $\Delta E$  decreases], thus explaining why our calculated energies for Pc<sup>4-</sup> and Pc<sup>5-</sup> are too large. A second factor that enters is configuration interaction (CI) between the Q state and other excited states. The various state symmetries are listed in Table IV. In all cases except the trianion there is CI between the Q

(29) Gouterman, M.; Wagniere, G. H. *J. Chem. Phys.* **1962**, *36*, 1188.  
(30) Fulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1961**, *35*, 1059.

(31) Vincett, P. S.; Voigt, E. M.; Rieckhoff, K. E. *J. Chem. Phys.* **1971**, *55*, 4131.

and the Soret states, which red shifts the Q band. However, in the monocation and dianion there is also CI between, respectively, the lower energy  $\pi$ - $\pi^*$  and the  $\pi^*$ - $\pi^*$  states and the Q state that cancels the red shift to some extent. In the trianion there is no CI between Q and Soret states so that there is less counterweight to CI with the lower energy  $\pi^*$ - $\pi^*$  states and the resultant blue shift. The net result is that the Q state in the neutral has an extra red shift with respect to the ionic species. The effect of CI in the monoanion is complicated by the fact that only some of the four Q states have CI with the lower energy  $\pi^*$ - $\pi^*$  states (Table IV). Overall, the CI effects on the energy would seem to be small.

Finally, can we correlate these results with electrochemical data? Consider that a well-defined pattern emerges<sup>7,16,17</sup> if one views the differences between reduction potentials of various species. Thus

$$\begin{aligned} E(\text{Pc}^-) - E(\text{Pc}^{2-}) &= \text{ca. } 1.6\text{--}1.7 \text{ eV} = \text{ca. } 13\,300 \text{ cm}^{-1} \\ E(\text{Pc}^{2-}) - E(\text{Pc}^{3-}) &= \text{ca. } 0.4 \text{ eV} = \text{ca. } 3200 \text{ cm}^{-1} \\ E(\text{Pc}^{3-}) - E(\text{Pc}^{4-}) &= \text{ca. } 0.6 \text{ eV} = \text{ca. } 4800 \text{ cm}^{-1} \\ E(\text{Pc}^{5-}) - E(\text{Pc}^{6-}) &= \text{ca. } 0.4 \text{ eV} = \text{ca. } 3200 \text{ cm}^{-1} \quad (9) \end{aligned}$$

It should be possible to calculate these differences in energy in terms of the optical parameters described above, by regrouping them in terms of the energy parameters used in the optical spectroscopy discussion. Thus, the energy,  $\Delta W$ , necessary to add an electron, in the gas phase, to the cation  $\text{Pc}^+$  is  $\epsilon_a$ , while the energy,  $\Delta W$ , necessary to reduce the neutral to the monoanion  $\text{Pc}^{3-}$ , also in the gas phase is  $\epsilon_r$ . Values for these and the other species are shown in column 3 of Table III. In solution it is necessary to take into account the difference in solvation energy of the two partners of the couple. These are related to the reduction potentials,  $E^\circ$ , following Hush<sup>21</sup> by

$$-FE^\circ - C = \Delta W + (n_f^2 - n_i^2)\alpha \quad (10)$$

Here,  $F$  is the Faraday constant,  $C$  is the constant that depends on the choice of reference electrode,  $n_i$  and  $n_f$  are the charges of initial and final species, and  $\alpha$  is the free energy of solvation of the monoanion and monocation, here considered an equal negative number. By taking differences in  $E^\circ$  values the arbitrary constant  $C$  is eliminated. From  $\Delta W$  and eq 10 we obtain expressions for the differences in (9),  $\Delta(-FE^\circ)$ , which are given in the fifth column of Table III in terms of the parameters in (8).

It was noted some time ago that the difference in redox potentials for oxidation and reduction of the neutral porphyrin corresponds approximately to the lowest  $\pi$ - $\pi^*$  transition energy.<sup>32</sup> Recently we<sup>33</sup> have explored the relationship involving the optical transition energy ( $E_{\text{op}}$ ) between the orbitals  $\Psi_g$  and  $\Psi_e$  in a complex and the difference in oxidation potential for oxidation at  $\Psi_g$  and reduction at  $\Psi_e$ ,  $\Delta E(\text{redox})$ .<sup>33,34</sup> This was written

$$E_{\text{op}} = \chi_i + nF(\Delta E(\text{redox})) + \Delta\Delta G_s + Q + \chi_o + \Delta(\text{solvn}) \quad (11)$$

where  $\chi_i$  and  $\chi_o$  are the inner (vibrational) and outer (solvation) reorganization energies,  $Q$  is the gas-phase self-quenching energy (ground-state molecule quenching of an excited-state molecule to yield the reduced and oxidized species as the electron transfer products),  $\Delta\Delta G_s = 2\Delta G_s - \Delta G_s^- - \Delta G_s^+$ ,  $\Delta(\text{solvn}) = \Delta G_s^* - \Delta G_s$ , and  $\Delta G_s$ ,  $\Delta G_s^*$ ,  $\Delta G_s^+$ , and  $\Delta G_s^-$  are the solvation free energies of the neutral ground state, excited state, cation, and anion, respectively.

We have previously noted<sup>6</sup> in comparing phthalocyanine redox potentials and electronic charge-transfer energies that the inner

reorganization energy is small because there are so many electrons that exciting one has little effect upon molecular dimensions. The outer reorganization energy is small because excitation of one of these many electrons, especially in this case, has little effect upon the solvation energy. Thus,  $\chi_i$  and  $\chi_o$  in (11) can be ignored. In this case it is necessary if  $E_{\text{op}} = nF(\Delta E(\text{redox}))$  that

$$-Q = \Delta\Delta G_s + \Delta(\text{solvn}) = \Delta G_s + \Delta G_s^* - \Delta G_s^+ - \Delta G_s^- \quad (12)$$

Within the terminology of Hush, we may write

$$2\alpha = -(\Delta\Delta G_s - \Delta G_s^+ - \Delta G_s^-) \quad (13)$$

but in the case of the phthalocyanines with such a large aromatic ring over which to delocalize the excited-state charge, it is probably a good approximation to write  $\Delta G_s^* = \Delta G_s$ . Further, the self-quenching energy may be written in terms of  $J$  and  $K$  integrals such that (12) becomes (14). With this substitution, an expression

$$-(\Delta G_s + \Delta G_s^* - \Delta G_s^+ - \Delta G_s^-) = 2\alpha = -J_{\text{ax}} + 2K_{\text{ax}} \quad (14)$$

for  $\Delta(-FE^\circ)$  can be written in terms of the various molecular  $J$  and  $K$  integrals, as shown in the sixth column of Table III. Using the numerical values from (8), we obtain the calculated values in the sixth column of Table III. The qualitative agreement between the experimental and calculated numbers (columns 5 and 6 of Table III) is remarkably good.

In writing eq 14, molecular integrals are being related to solvation energy. At first thought this seems rather unlikely, as the one quantity is intramolecular and the other is intermolecular. However, although there has not been much systematic study, it appears that the Pc-ring redox potentials  $E^\circ$  have little solvent dependence and their differences even less. This is in spite of the term  $2\alpha$  appearing in  $\Delta(-FE^\circ)$  (Table III, column 5).

We conclude that (i) the high degree of regularity in the spectra of the many redox species from one metal to another, and the ability to fit the spectra with parameters whose values are most reasonable, must provide confidence in the veracity of the assignments, (ii) species whose spectra are inconsistent must have anomalous redox behavior, (iii) following from these arguments, the electronic spectra of any Pc species in the redox range  $\text{Pc}^{6-}$  to  $\text{Pc}^-$  can now reasonably be characterized by its electronic spectrum (supported where possible with associated ESR data etc), and (iv) as previously seen in the discussion of the CT energies in transition-metal Pc species,<sup>6</sup> there is a good correlation between Pc electronic spectroscopy and electrochemical behavior. The configurational mixing of the Q and Soret states is certainly smaller than in the porphyrins, where this mixing is considerable.<sup>8,9</sup> It is this purity in the Q state that probably contributes in a major fashion to the success of this simple treatment, to the success previously seen in correlating CT energies, and to the simple correlations that can be drawn between electronic spectroscopy and electrochemistry.

**Acknowledgment.** This is part of a joint study in collaboration with Prof. A. J. Bard (University of Texas at Austin) and is funded by the Office of Naval Research (Washington, DC) to whom we are indebted. We are also indebted to the Natural Sciences and Engineering Research Council of Canada (Ottawa) for financial support. M.G. received partial support from NSF Grant DMR-7823958. We also thank Dr. E. S. Dodsworth for useful discussions.

**Registry No.** [ $\text{Co}^{\text{III}}\text{Pc}^-$ ]<sup>2+</sup>, 60482-88-4; [ $\text{Co}^{\text{III}}\text{Pc}^{2-}$ ]<sup>+</sup>, 18756-59-7; [ $\text{Co}^{\text{II}}\text{Pc}^{2-}$ ], 3317-67-7; [ $\text{Co}^{\text{I}}\text{Pc}^{2-}$ ]<sup>-</sup>, 18974-06-6; [ $\text{Cr}^{\text{III}}\text{Pc}^-$ ]<sup>2+</sup>, 95865-87-5; [ $\text{Cr}^{\text{III}}\text{Pc}^{2-}$ ]<sup>+</sup>, 47822-83-3; [ $\text{Zn}^{\text{II}}\text{Pc}^-$ ]<sup>+</sup>, 53029-44-0; [ $\text{Si}^{\text{IV}}\text{Pc}^-$ ]<sup>3+</sup>, 95865-88-6; [ $\text{Fe}^{\text{III}}\text{Pc}^-$ ]<sup>2+</sup>, 95865-89-7; [ $\text{Fe}^{\text{III}}\text{Pc}^{2-}$ ]<sup>+</sup>, 34808-44-1; [ $\text{Fe}^{\text{II}}\text{Pc}^{2-}$ ], 132-16-1; [ $\text{Fe}^{\text{I}}\text{Pc}^{2-}$ ], 38600-22-5; [ $\text{Mg}^{\text{II}}\text{Pc}^{2-}$ ], 1661-03-6; [ $\text{Ni}^{\text{II}}\text{Pc}^{2-}$ ], 14055-02-8; [ $\text{AlAlPc}^{2-}$ ], 14154-42-8; [ $\text{Mn}^{\text{II}}\text{Pc}^{2-}$ ], 14325-24-7; [ $\text{Zn}^{\text{II}}\text{Pc}^{2-}$ ], 14320-04-8; [ $\text{MgPc}^{3-}$ ]<sup>2+</sup>, 32458-93-8; [ $\text{MgPc}^{4-}$ ]<sup>2+</sup>, 34465-04-8; [ $\text{MgPc}^{5-}$ ]<sup>2+</sup>, 34465-05-9; [ $\text{MgPc}^{6-}$ ]<sup>4-</sup>, 34465-06-0; [ $\text{ClAlPc}^{3-}$ ]<sup>-</sup>, 38496-96-7; [ $\text{ClAlPc}^{4-}$ ]<sup>2-</sup>, 38548-71-9; [ $\text{ClAlPc}^{5-}$ ]<sup>2-</sup>, 38496-97-8; [ $\text{ClAlPc}^{6-}$ ]<sup>14-</sup>, 38496-98-9; [ $\text{ZnPc}^{3-}$ ]<sup>-</sup>, 38496-99-0; [ $\text{ZnPc}^{4-}$ ]<sup>2-</sup>, 38497-00-6; [ $\text{ZnPc}^{5-}$ ]<sup>3-</sup>, 38497-01-7; [ $\text{ZnPc}^{6-}$ ]<sup>4-</sup>, 38497-02-8; [ $\text{NiPc}^{3-}$ ]<sup>-</sup>, 38497-03-9; [ $\text{NiPc}^{4-}$ ]<sup>2-</sup>, 38530-22-2; [ $\text{NiPc}^{5-}$ ]<sup>3-</sup>, 38497-04-0; [ $\text{NiPc}^{6-}$ ]<sup>4-</sup>, 38741-74-1; [ $\text{Co}^{\text{I}}\text{Pc}^{3-}$ ]<sup>2-</sup>, 38530-24-4; [ $\text{Co}^{\text{I}}\text{Pc}^{4-}$ ]<sup>3-</sup>, 38530-25-5; [ $\text{Co}^{\text{I}}\text{Pc}^{5-}$ ]<sup>4-</sup>, 38497-05-1; [ $\text{Co}^{\text{I}}\text{Pc}^{6-}$ ]<sup>5-</sup>, 38600-21-4; [ $\text{MnPc}^{3-}$ ]<sup>-</sup>, 38600-24-7; [ $\text{MnPc}^{4-}$ ]<sup>2-</sup>, 38641-41-7; [ $\text{MnPc}^{5-}$ ]<sup>3-</sup>, 38600-25-8; [ $\text{MnPc}^{6-}$ ]<sup>5-</sup>, 38498-33-8.

(32) Fuhrhop, J. H. *Struct. Bonding (Berlin)* **1974**, 18, 1.

(33) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1984**, 112, 567.

(34) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, 22, 224.

(35) Minor, P. C.; Lever, A. B. P., unpublished observations.

(36) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, 7, 27; and this work.

(37) Lever, A. B. P.; Melnik, M.; Nevin, A.; Liu, W., unpublished observations.