

## ELECTROCHEMISTRY AND SPECTROELECTROCHEMISTRY OF STRONGLY ELECTRON-WITHDRAWING METALLATED OCTANITROPHTHALOCYANINES

Yu-Hong TSE<sup>a1</sup>, Nagao KOBAYASHI<sup>b</sup> and A. B. P. LEVER<sup>a2,\*</sup>

<sup>a</sup> Department of Chemistry, York University, 4700 Keele St., North York, Ontario, Canada, M3J-1P3; e-mail: <sup>1</sup> yht40761@gsk.com, <sup>2</sup> blever@yorku.ca

<sup>b</sup> Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan; e-mail: nagaok@mail.cc.tohoku.ac.jp

Received November 23, 2000

Accepted January 15, 2001

*Dedicated to Professor Antonín A. Vlček, a dear friend, a mentor of electrochemistry and a creative scientist.*

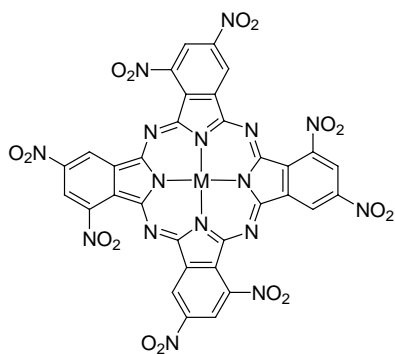
The spectral and electrochemical properties of metallated octanitrophthalocyanines,  $[M^{II}\{(NO_2)_8pc\}]$  where M = Zn, Cu or Co, were studied by electrochemical and spectroelectrochemical methods as well as electronic absorption and magnetic circular dichroism spectroscopy. Aggregation is observed for several species. The octanitrophthalocyanines are easier to reduce and more difficult to oxidize than most other metallophthalocyanines. Indeed, the first ring-localized reduction potential observed with these phthalocyanine species, is the most positive of the metallated, neutral phthalocyanines in the literature. These data are added to existing Hammett free energy relationship database to extend design protocols for substituted metallophthalocyanines. Optical spectra for several redox series are presented and related to the existing literature.

**Keywords:** Phthalocyanines; Electrochemistry; Electronic absorption spectroscopy; Zinc; Copper; Cobalt; Metallophthalocyanines; Substituents effects.

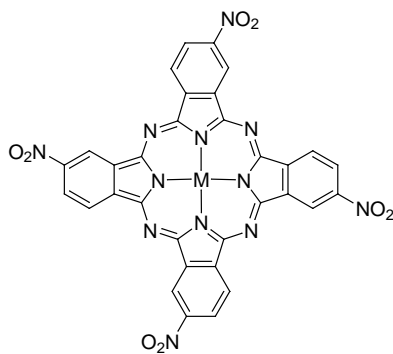
Phthalocyanines (pc) have had an established importance in industrial applications for more than half a century<sup>1-3</sup>. Early in the 20th century, they were extensively employed as dyestuffs in paints, textiles and plastics because of their intense dark green or blue colour, chemical stability and photostability. More recently, studies of phthalocyanines have been extended to many important technological applications, such as in chemical sensors, electrocatalysis, photodynamic (cancer) therapy, molecular electronic devices, photovoltaics, information storage, *etc.* Current non-paint

commercial use includes their application in photocopying machines, CD write disks and as an infrared ink for security purposes<sup>4</sup>.

The technological value of metallophthalocyanines (Mpc) is based on several distinctive properties, in particular their intense light absorption and multiple redox activity. These properties are tunable over a wide range by varying the metal centre and by substitution of the phthalocyanine ring. Together with the replacement of the benzene ring in metallophthalocyanines with naphthalene, anthracene, *etc.*, possible variations of the basic metallophthalocyanine skeleton are essentially limitless yet the fundamental properties of intense light absorption and extensive redox activity can be retained. Here we explore properties of metallated octanitrophthalocyanines with special interest in exploring how these strongly electron attracting groups influence redox activity. There is also interest in providing protocols for the design of new metallophthalocyanines. This can be achieved through the use of Hammett substituent constants and ligand electrochemical parameters<sup>4,5</sup>. The nitro group has one of the most positive Hammett constants<sup>6</sup>. Thus, another objective of this publication is to extend a previous Hammett analysis of metallophthalocyanines<sup>7</sup>. Electrochemical properties of tetranitrophthalocyanine derivatives have been fairly well studied<sup>8-11</sup>, but little is known<sup>12-15</sup> of the electrochemical behaviour of octanitrophthalocyanine species. We also carried out spectroelectrochemical experiments to record optical spectra of the redox series of oxidized and reduced polynitrophthalocyanine species. The resulting spectra are compared with spectroscopic data for related species found in the literature.



Octanitrophthalocyanine complexes  
[M<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}] (M = Zn, Cu, Co)



Tetranitrophthalocyanine complex  
[Co<sup>II</sup>{(NO<sub>2</sub>)<sub>4</sub>pc}]

## EXPERIMENTAL

### Materials

Tetrabutylammonium perchlorate (TBAP; Kodak) was recrystallized from absolute ethanol and dried in a vacuum oven at 50 °C for 2 days. Dimethylformamide (DMF; Aldrich) was used as supplied. Dimethyl sulfoxide (DMSO) was dried with molecular sieves and distilled under vacuum before use. Argon gas or nitrogen (Linde) were used as supplied.

### Methods

Differential pulse voltammetry (DPV) was performed with a Princeton Applied Research (PAR) Model 174A polarographic analyzer or a Model CS-900-UPG Computer Controlled Electroanalysis System (Cypress System, Inc., software version 5.0). Cyclic voltammetry was performed with a Pine Instrument RDE-3 potentiostat. A conventional three electrode cell was used in electrochemical experiments. A platinum (Pt) disk with the cross-sectional area of 0.196 mm<sup>2</sup>, sealed in glass, was used as the working electrode; a Pt wire was the counter electrode, and an AgCl/Ag wire served as the pseudoreference electrode. Potentials were referenced internally to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple. In this work, all the potentials are reported against the SCE reference electrode and the Fc/Fc<sup>+</sup> potential is set at 0.5 V vs SCE in DMSO (ref.<sup>16</sup>).

The spectroelectrochemical thin-layer cell followed the design by Krejčík *et al.*<sup>17</sup>. The AgCl/Ag electrode inside the spectroelectrochemical cell may deviate slightly from its true thermodynamic value. Electronic absorption spectra were recorded during the spectroelectrochemical experiments with a Cary Model 2400 spectrophotometer.

Electronic absorption spectra of non-electrolyzed solutions were recorded with a Hitachi 330LC spectrophotometer, and magnetic circular dichroism (MCD) measurements were made using a JASCO J-725 spectrodichrometer with a JASCO electromagnet which produces magnetic fields as great as 1.09 T, with parallel and anti-parallel fields. Their magnitude was expressed in terms of molar ellipticity per Tesla ( $[\Theta]_M$ , deg dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> T<sup>-1</sup>).

### Syntheses

Cobalt tetranitrophthalocyanine, [Co<sup>II</sup>{(NO<sub>2</sub>)<sub>4</sub>pc}], was synthesized according to a literature procedure<sup>18</sup>. Copper and cobalt octanitrophthalocyanines were prepared by literature procedures<sup>12,14,15</sup>. The complexes were analytically pure.

*[Co{(NO<sub>2</sub>)<sub>8</sub>pc}]*: For C<sub>32</sub>H<sub>8</sub>N<sub>16</sub>O<sub>16</sub>Co (931.5) calculated: 41.26% C, 0.87% H, 24.06% N; found: 40.70% C, 1.04% H, 24.42% N.

*[Cu{(NO<sub>2</sub>)<sub>8</sub>pc}]*: For C<sub>32</sub>H<sub>8</sub>N<sub>16</sub>O<sub>16</sub>Cu (936.1) calculated: 41.06% C, 0.86% H, 23.94% N; found: 40.57% C, 1.10% H, 24.40% N.

*Zinc octanitrophthalocyanine*. 3,5-Dinitrophthalonitrile (109 mg, 0.5 mmol) was heated with lithium methoxide (5 mg, 0.13 mmol) at 180–190 °C for 2 h. DMF (2 cm<sup>3</sup>) and dried zinc acetate (ca 100 mg) were added to the reaction mixture and heated at 150–160 °C under nitrogen in the dark for 6 h. After cooling, water (10 cm<sup>3</sup>) was added and the resulting precipitate was collected by filtration, washed with water and methanol. The residue was dissolved in the least amount of DMSO and water was added to cause precipitation. The product was collected by filtration and dried to yield 41 mg (35%) of the desired

[Zn{(NO<sub>2</sub>)<sub>8</sub>pc}]. For C<sub>32</sub>H<sub>8</sub>N<sub>16</sub>O<sub>16</sub>Zn (937.9) calculated: 40.98% C, 0.86% H, 23.89% N; found: 40.37% C, 0.90% H, 23.42% N.

## RESULTS AND DISCUSSION

### *Electrochemistry*

Electrochemical properties of metallophthalocyanines are well known<sup>16</sup>. In principle, we can expect redox reactivity at both the metal ion and the phthalocyanine ring. In the latter case, it is usually possible to observe at least two ring-localized oxidation processes and often as many as four (or more) ring-localized reduction processes. In the case of copper(II) and zinc(II) species, metal redox processes are not observed (but *vide infra*), while for cobalt(II) species both oxidation to cobalt(III) and reduction to cobalt(I) complexes can often be identified; these usually (but not always) occur before ring oxidation and reduction, respectively. Oxidation to Co<sup>III</sup>pc species is affected by solvent and supporting electrolyte ions<sup>16</sup>. Specifically, donor solvents (D) favour formation first of [Co<sup>III</sup>(pc)D<sub>2</sub>] species<sup>19</sup>, while non-donor solvents favour formation first of a [Co<sup>II</sup>{pc(1-)}] species<sup>16,20,21</sup>. The [M<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}] species are fairly soluble in both DMF and DMSO. However, these species display properties of aggregation<sup>21-29</sup> in these solvents. The cyclic voltammograms (CV) obtained from these phthalocyanine solutions, commonly consist of overlapping waves due to the diffusion of monomeric and polymeric species; it is very difficult to derive accurate  $E_{1/2}$  values from these CV data. Differential pulse voltammetry (DPV) (Fig. 1), however, yields data from which  $E_{1/2}$  values are more readily determined (as averages of forward and reverse scan potentials) and which are tabulated (Table I).

We present first the DPV data and assignments of the couples which are further confirmed by subsequent discussion of the spectroelectrochemical behaviour.

### [Zn<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}]

No oxidation process was discerned in the DPV of [Zn<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}] but four reduction processes could be observed prior to the solvent limit. Since the Zn(II) metal centre is not redox-active, these reduction processes are assigned specifically as Znpc(2-)/Znpc(3-), Znpc(3-)/Znpc(4-), Znpc(4-)/Znpc(5-) and Znpc(5-)/Znpc(6-), respectively. At a concentration of  $1.1 \cdot 10^{-4}$  mol dm<sup>-3</sup> (see Fig. 1d and Table I), the first reduction process, Znpc(2-)/Znpc(3-), shows two DPV signals, labeled as II<sub>agg</sub> and II, in the potential range from

0.2 to  $-0.2$  V. When the concentration of  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  is decreased to  $7 \cdot 10^{-6}$  mol  $\text{dm}^{-3}$ , only one differential pulse signal is observed at a potential close to that of II (see Fig. 1d and Table I), confirming that the process  $\text{II}_{\text{agg}}$  involves the first reduction of the aggregated  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  species. Similar observations have been reported and discussed in detail for the zinc octacyanophthalocyanine<sup>30</sup>,  $[\text{Zn}^{\text{II}}\{(\text{CN})_8\text{pc}\}]$ .

### $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$

The DPV of the  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  complex behaves similarly to that of  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  (see Fig. 1c and Table I). Four reduction processes are also observed; however, only one DPV wave is recorded for the first reduction process. The three most negative processes are assigned as reduction processes involving the phthalocyanine ring. However, there is some uncertainty about the site of the reduction for the first process; we return to this below in the spectroelectrochemistry section. Decreasing the concentration of  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  from  $1.6 \cdot 10^{-3}$  to  $6 \cdot 10^{-6}$  mol  $\text{dm}^{-3}$  does not change the appearance of the DPV significantly. Thus, aggregation is not a significant factor for this species.

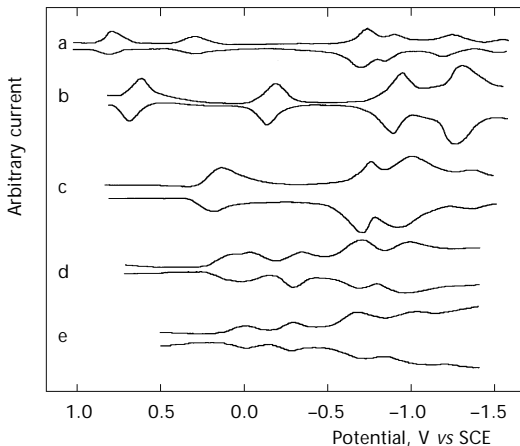


FIG. 1

Differential pulse voltammograms for nitrophthalocyanine species in DMSO/ $1 \cdot 10^{-1}$  M TBAP, Pt working electrode. a  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 1.4 \cdot 10^{-3}$  mol  $\text{dm}^{-3}$ ; b  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}] = 6.3 \cdot 10^{-5}$  mol  $\text{dm}^{-3}$ ; c  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 1.6 \cdot 10^{-3}$  mol  $\text{dm}^{-3}$ ; d  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 1.1 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$ ; e  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 7 \cdot 10^{-6}$  mol  $\text{dm}^{-3}$ . In each pair, the top scan is forward from left to right and the lower scan is backward from right to left. All the waves are net reduction processes except for the left-most waves in a and b



The DPV of  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  species (Fig. 1a) shows one oxidation and four reduction processes, *i.e.* the open circuit potential lies between processes I and II (Table I). The oxidation and first reduction processes are assigned to  $\text{Co}^{\text{III}}\text{pc}/\text{Co}^{\text{II}}\text{pc}$  and  $\text{Co}^{\text{II}}\text{pc}/\text{Co}^{\text{I}}\text{pc}$  couples, respectively, following the extensive previous literature<sup>16</sup>. The other three reduction processes that occur over the potential range of  $-0.5$  to  $-1.3$  V, are assigned to the consecutive reduction of the phthalocyanine ring.



In order to compare the effect of the number of nitro groups on the redox potentials of a phthalocyanine, the electrochemical behaviour of the  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$  species was re-investigated<sup>8-11</sup>. One oxidation and three re-

TABLE I  
Redox potentials,  $E_{1/2}$ , of metallated nitrophthalocyanines<sup>a</sup>

$[\text{M}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$	Oxidation				Reduction			
	I	II <sub>agg</sub>	II	III <sub>agg</sub>	III	IV	V	VI
M = Co <sup>b</sup>	0.82		0.31		-0.68	-0.83	-1.20	
M = Cu <sup>c</sup>					0.21	-0.71	-0.95	-1.30
M = Zn <sup>d</sup>				0.10	0.02	-0.31	-0.69	-0.96
M = Zn <sup>e</sup>					0.01	-0.28	-0.66	-1.05
$[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$								
<sup>f</sup>	0.65	0.06	-0.21		-0.93	-1.32		
<sup>g</sup>	0.65		-0.15		-0.91	-1.27		
$[\text{Co}^{\text{II}}(\text{TNpc})^h$	0.38		-0.45		-1.59			
$[\text{Zn}\{(\text{CN})_8\text{pc}\}]^i$					-0.15	-0.50	-1.10	-1.35
$[\text{Zn}(\text{TNpc})^j$	0.45 <sup>k</sup>				-1.03	-1.45		

<sup>a</sup> For new data in this work, these values are the average potentials of forward and reverse DPV peak potentials; DMSO/ $1 \cdot 10^{-1}$  mol dm<sup>-3</sup> TBAP, V vs SCE; I: Co(III)/Co(II); II: Co(II)/Co(I); III: pc(2-)/pc(3-); IV: pc(3-)/pc(4-); V: pc(4-)/pc(5-); VI: pc(5-)/pc(6-). <sup>b</sup>  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 1.4 \cdot 10^{-3}$  mol dm<sup>-3</sup>. <sup>c</sup>  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 1.6 \cdot 10^{-3}$  mol dm<sup>-3</sup>. <sup>d</sup>  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 1.1 \cdot 10^{-4}$  mol dm<sup>-3</sup>. <sup>e</sup>  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}] = 7 \cdot 10^{-6}$  mol dm<sup>-3</sup>. <sup>f</sup>  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}] = 1.5 \cdot 10^{-3}$  mol dm<sup>-3</sup>. <sup>g</sup>  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}] = 6.3 \cdot 10^{-5}$  mol dm<sup>-3</sup>. <sup>h</sup> From ref.<sup>40</sup>, in DMF. <sup>i</sup> From ref.<sup>30</sup>. <sup>j</sup> From ref.<sup>55</sup>. <sup>k</sup> Zn{pc(1-)/Zn{pc(2-)} process in DMF.

duction processes were observed for  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$  species at a concentration of  $6.3 \cdot 10^{-5} \text{ mol dm}^{-3}$  (see Fig. 1b, Table I), with similar assignments to that for the  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  species. Increasing the concentration of the solution to  $1.5 \cdot 10^{-3} \text{ mol dm}^{-3}$  again leads to two DPV signals for the Co(II)/Co(I) redox couple (Table I), indicative of a similar aggregation process to that observed with  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  species at a high concentration.

### Electronic Absorption Spectra

#### UV-VIS Spectroscopy and Magnetic Circular Dichroism of the Parent Species

Figures 2a–2c show the absorption and MCD spectra of  $[\text{M}\{(\text{NO}_2)_8\text{pc}\}]$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ ) in DMSO. In this solvent,  $[\text{Zn}\{(\text{NO}_2)_8\text{pc}\}]$  is monomeric but a split Q band is still observed. This may well arise from a non-axially symmetric conformation of the nitro groups whose  $\pi$ -levels are likely to be quite strongly mixed with the phthalocyanine  $\pi$ -levels. Compared with the Q and Soret bands of  $[\text{Zn}(\text{pc})]$  without peripheral substituents<sup>31,32</sup>, these bands lie at longer wavelengths by *ca* 40 and 70–80 nm, respectively, as the result of octanitro substitution. In particular, the Soret band (at *ca* 410–415 nm, judging from the dispersion type MCD curve) lies at the longest wavelength among various substituted Zn(pc) complexes reported to date. The MCD intensity of the Soret band, which is about one order of magnitude smaller than that of the Q band<sup>33</sup>, also infers that  $[\text{Zn}\{(\text{NO}_2)_8\text{pc}\}]$  exists as a monomer.

The spectra of  $[\text{Co}\{(\text{NO}_2)_8\text{pc}\}]$  and  $[\text{Cu}\{(\text{NO}_2)_8\text{pc}\}]$  are those of aggregated species<sup>21,23–28,33</sup>, in agreement with the electrochemical data discussed above. The broad spectra generally agree with the data reported by Achar and Bhandari<sup>12</sup>, but the structure in our  $[\text{Co}\{(\text{NO}_2)_8\text{pc}\}]$  spectrum is absent from the Achar spectrum. There is much better agreement with the data reported for the cobalt species by Negrimovskii *et al.*<sup>14</sup>, though there are differences in energy in the Q band region. In view of the aggregation exhibited by these species, the differences between the spectra reported by us and those cited in the literature are probably due to differences in the concentrations used. For both compounds, the absorption coefficients of the Soret band are apparently larger than those of the broad and structureless Q band. The broad negative-to-positive MCD pattern viewing from the longer wavelength also confirms that these compounds are aggregated to some extent in DMSO.

## Spectroelectrochemical Studies

An optically transparent thin-layer electrochemical cell<sup>17</sup> was used to carry out controlled-potential electrolysis studies to obtain optical spectra of various redox products. The potential was generally held approximately 200 mV positive (for oxidation) or negative (for reduction) of a specific

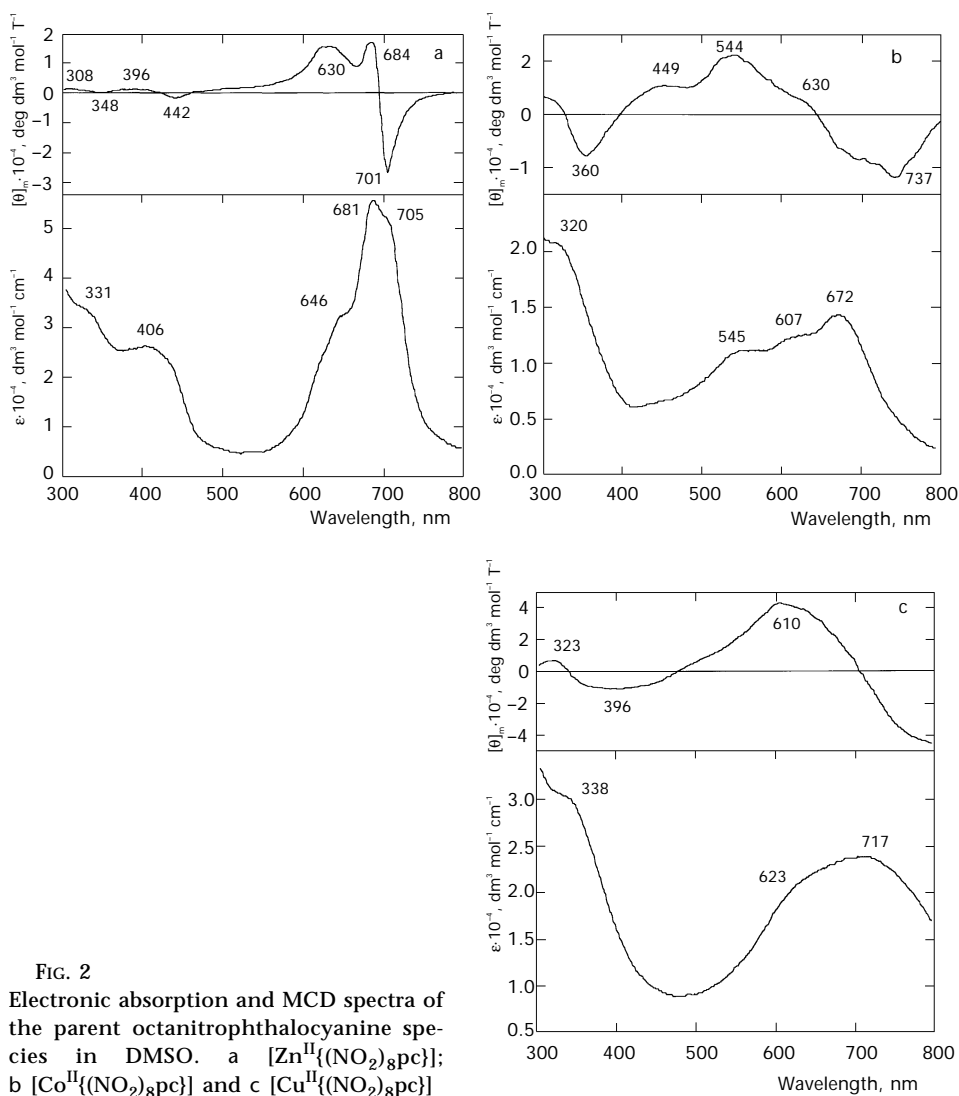


FIG. 2  
 Electronic absorption and MCD spectra of the parent octanitrophthalocyanine species in DMSO. a [Zn<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}]; b [Co<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}] and c [Cu<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}]



process until the electronic spectrum showed no further changes. Figures 3 and 4 illustrate the time development of the spectra of the various species. At the end of each experiment, the potential was reversed to approximately

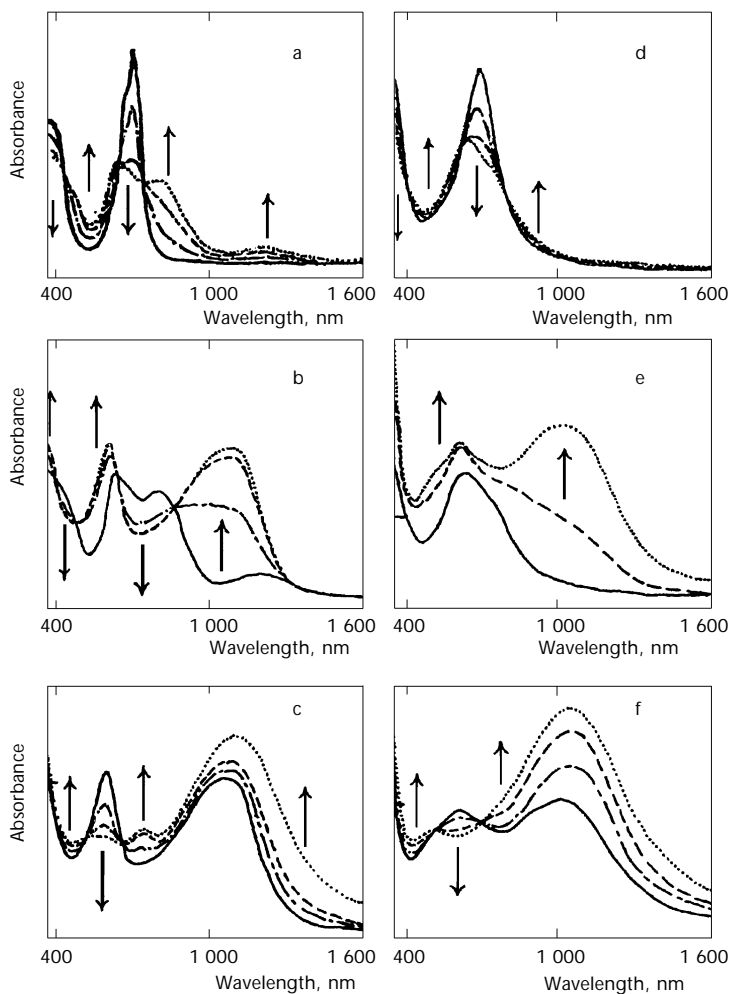


FIG. 3

Spectroscopic changes, as a function of time, during the formation of reduced octanitrophthalocyanine species in DMSO/ $2 \cdot 10^{-1}$  mol dm<sup>-3</sup> TBAP, under controlled-potential electrolysis conditions. Panels a, b and c show the formation of  $[\text{Zn}\{(\text{NO}_2)_8\text{pc}(3-)\}]^-$ ,  $[\text{Zn}\{(\text{NO}_2)_8\text{pc}(4-)\}]^{2-}$  and  $[\text{Zn}\{(\text{NO}_2)_8\text{pc}(5-)\}]^{3-}$  from the parent  $[\text{Zn}\{(\text{NO}_2)_8\text{pc}\}]$  complex, respectively. Panels d, e and f show the formation of  $[\text{Cu}^{\text{I}}\{(\text{NO}_2)_8\text{pc}\}]^-$  (see text),  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(4-)\}]^{2-}$  and  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(5-)\}]^{3-}$  from the parent  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  complex, respectively

the open circuit potential to recover the original non-oxidized or non-reduced bulk species, thereby proving the reversibility of the oxidation or reduction process. In most cases, except where noted below, reversibility was demonstrated. The electronic spectra of metallophthalocyanine reduced species have been fairly extensively studied<sup>31,34-45</sup>. Small differences in the spectra of parent species between Figs 2a-2c and Figs 3 and 4 are probably due to differences in concentration (and hence degree of aggregation) and the fact that there is supporting electrolyte present in the solution for the data shown in Figs 3 and 4 but not for the data in Fig. 2.

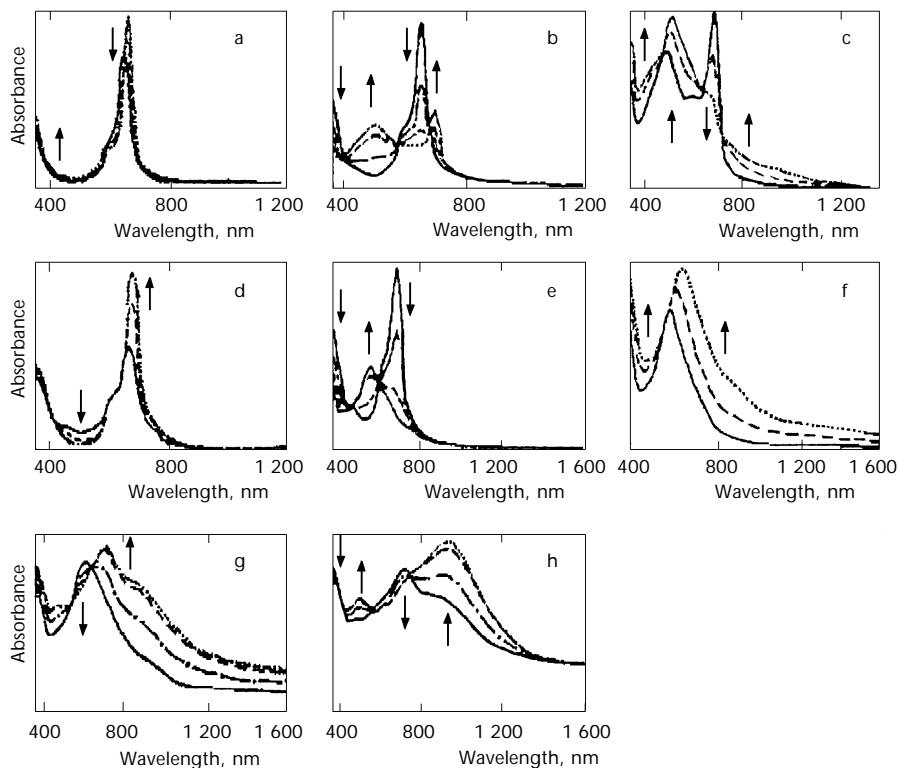


FIG. 4

Spectroscopic changes, as a function of time, during the formation of oxidized and reduced nitrophthalocyanine species in  $\text{DMSO}/2 \cdot 10^{-1} \text{ mol dm}^{-3}$  TBAP, under controlled-potential electrolysis conditions. Panels a, b and c show the formation of  $[\text{Co}^{\text{III}}\{(\text{NO}_2)_4\text{pc}\}]^+$ ,  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_4\text{pc}\}]^-$  and  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_4\text{pc}(3-)\}]^{2-}$  from the parent  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$  complex, respectively. Panels d, e, f, g and h show the formation of  $[\text{Co}^{\text{III}}\{(\text{NO}_2)_8\text{pc}\}]^+$ ,  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}\}]^-$ ,  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(3-)\}]^{2-}$ ,  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(4-)\}]^{3-}$  and  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(5-)\}]^{4-}$  from the parent  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  complex, respectively



*pc(3-) radical anion:* The spectroscopic changes accompanying the reduction of  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  to its *pc(3-)* radical anion are shown in Fig. 3a. The resulting splitting of the parent Q band into two intense peaks at 12 760 and 16 160  $\text{cm}^{-1}$  (Table II), and the growth of a weak and broad absorbance in the NIR region (8 380  $\text{cm}^{-1}$ ), are typical of the formation of a phthalocyanine *pc(3-)* radical anion<sup>34,35,37,38,43</sup>. The electron-withdrawing

TABLE II

Electronic absorption spectra of  $[\text{M}\{(\text{NO}_2)_x\text{pc}\}]$  ( $x = 8$ ,  $\text{M} = \text{Zn}$ ,  $\text{Cu}$ ,  $\text{Co}$ ;  $x = 4$ ,  $\text{M} = \text{Co}$ ) complexes and their oxidized and reduced forms<sup>a,b</sup>

Neutral species	Co(III)	Co(I)	<i>pc(3-)</i>	<i>pc(4-)</i>	<i>pc(5-)</i>
$[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$			$\text{Zn}^{\text{II}}\{\text{pc}(3-)\}^-$	$\text{Zn}^{\text{II}}\{\text{pc}(4-)\}^{2-}$	$\text{Zn}^{\text{II}}\{\text{pc}(5-)\}^{3-}$
701 (sh)			1 193	1 069 (s,br)	1 103 (s,br)
686			784	985 (sh)	738
406, 331 (sh)			619	598	538
$[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$			$\text{Cu}^{\text{II}}\{\text{pc}(3-)\}^-$	$\text{Cu}^{\text{II}}\{\text{pc}(4-)\}^{2-}$	$\text{Cu}^{\text{II}}\{\text{pc}(5-)\}^{3-}$
717 br			1 190 (w)	1 041 (s,br)	1 046 (s,br)
623 (sh)			1 087 (w)	612	514
338 (sh)			768 (sh)	514 (sh)	
			627		
$[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$	$\text{Co}^{\text{III}}(\text{pc})^+$	$\text{Co}^{\text{I}}(\text{pc})^-$	$\text{Co}^{\text{I}}\{\text{pc}(3-)\}^{2-}$	$\text{Co}^{\text{I}}\{\text{pc}(4-)\}^{3-}$	$\text{Co}^{\text{I}}\{\text{pc}(5-)\}^{4-}$
672	691	543	1 245 (w)	873 (sh)	916
602 (sh)	617 (sh)		889 (sh)	705	479
545 (sh)			609	476 (sh)	
406, 331					
$[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$	$\text{Co}^{\text{III}}(\text{pc})^+$	$\text{Co}^{\text{I}}(\text{pc})^-$	$\text{Co}^{\text{I}}\{\text{pc}(3-)\}^{2-}$		
653	667	701	908 (w)		
594 (sh)	602 (sh)	631	689 (sh)		
		500	527		
		435 (sh)	444 (sh)		

<sup>a</sup>  $\text{DMSO}/2 \cdot 10^{-1} \text{ mol dm}^{-3}$  TBAP. <sup>b</sup> Data are wavelengths in nm; sh = shoulder, s = strong, br = broad, w = weak.

group appears to shift the double band system to lower energy relative to that seen<sup>35,42</sup> in the spectra of  $[\text{Zn}\{\text{pc}(3-)\}]^-$  and  $[\text{Mg}\{\text{pc}(3-)\}]^-$  and other metallophthalocyanine(3-) species.

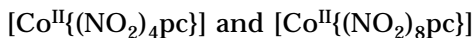
*pc(4-) anion:* The spectroscopic changes during the reduction of  $[\text{Zn}^{\text{II}}\{\text{pc}(3-)\}]^-$  to  $[\text{Zn}^{\text{II}}\{\text{pc}(4-)\}]^{2-}$  are shown in Fig. 3b (Table II). The resulting spectra compare reasonably well with the spectral data for  $[\text{Mg}^{\text{II}}\{\text{pc}(4-)\}]^{2-}$  (refs<sup>34,37</sup>),  $[\text{Zn}^{\text{II}}\{\text{Cl}_{16}\text{pc}(4-)\}]^{2-}$  (ref.<sup>43</sup>) and  $[\text{Zn}^{\text{II}}\{\text{pc}(4-)\}]^{2-}$  (ref.<sup>38</sup>), but are again shifted to the red and the broad band obscures some features observable in the spectrum of the  $[\text{Mg}\{\text{pc}(4-)\}]^{2-}$  ion<sup>37</sup>. In particular, the weak bands usually appearing beyond *ca* 750 nm, are obscured.

*pc(5-) radical anion:* The spectroscopic changes during the reduction of the  $[\text{Zn}^{\text{II}}\{\text{pc}(4-)\}]^{2-}$  to the  $[\text{Zn}\{\text{pc}(5-)\}]^{3-}$  species are shown in Fig. 3c. The presumed Q band shifts to the red and the intensity of the NIR transition increases. Further reduction results in the decomposition of the starting material.



*First reduction step:* Figure 3d shows spectral changes for the formation of the 1e-reduced species. Only one principal transition is observed at 627 nm. This spectrum is rather different from those of  $[\text{Cu}^{\text{II}}\{\text{pc}(3-)\}]^-$  (ref.<sup>39</sup>) and copper tetrasulfophthalocyanine  $[\text{Cu}^{\text{II}}\{\text{Tspc}(3-)\}]^-$  (ref.<sup>46</sup>) that show two strong Q bands in the 500–700 nm region. It also differs from the other pc(3-) spectra reported herein. The spectrum indeed appears more like a metallophthalocyanine(2-) spectrum. The NIR bands expected for a pc(3-) species are apparently not present. However, similar spectroscopic characteristics have been reported for the first reduction product of the  $[\text{Cu}^{\text{II}}\{(\text{CN})_8\text{pc}\}]$  species<sup>44,47a</sup>. It is feasible that in these species containing highly withdrawing substituents ( $\text{CN}^-$  and  $\text{NO}_2$ ), reduction of the metal centre to  $\text{Cu}^{\text{I}}(\text{pc})$  is thermodynamically more accessible than formation of  $\text{Cu}^{\text{II}}\{\text{pc}(3-)\}$ . Indeed, this has been proposed on the basis of the Raman spectrum of a thin film of reduced  $[\text{Cu}\{(\text{CN})_8\text{pc}\}]$  (ref.<sup>47b</sup>).

*pc(4-) and pc(5-) anions:* Figures 3e and 3f show spectral changes during the formation of  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(4-)\}]^{2-}$  and  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(5-)\}]^{3-}$ , respectively. The resulting electronic spectra are very similar, indeed, to the spectra of the corresponding  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(4-)\}]^{2-}$  and  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(5-)\}]^{3-}$  complexes, confirming these assignments.



*Co<sup>III</sup>(pc)<sup>+</sup>:* Figures 4a and 4d show spectral changes during the oxidation of  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$  and  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  in DMF solution, respectively.

These spectra are characterized by a small shift in energy to the red, an increase in intensity and a sharpening of the Q band, which are typical characteristics of oxidation to a  $\text{Co}^{\text{III}}\text{pc}$  species<sup>40,48</sup>. Similar spectra for  $\text{Co}^{\text{III}}\text{pc}$  have been reported for  $[\text{Co}^{\text{III}}(\text{pc})\text{X}_2]^-$  ( $\text{X} = \text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$  or  $\text{Br}^-$ ) (ref.<sup>49</sup>),  $[\text{Co}^{\text{III}}(\text{TNpc})(\text{DMF})_2]^+$  (ref.<sup>40</sup>),  $[\text{Co}^{\text{III}}(\text{pc})(\text{CN})_2]^-$  (ref.<sup>49</sup>) and  $[\text{Co}^{\text{III}}(\text{TNpc})(\text{CN})_2]^-$  (ref.<sup>40</sup>) complexes; TNpc = tetra(neopentyloxy)phthalocyanine.

$\text{Co}^{\text{I}}(\text{pc})^-$ : Polarization of a solution of  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_4\text{pc}\}]$  or  $[\text{Co}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  just negative of the first reduction wave results in the formation of a  $\text{Co}^{\text{I}}(\text{pc})^-$  species (Figs 4b and 4e, Table II). The UV-VIS spectra of the latter anion are characterized by the appearance of a strong band at *ca* 500 nm, assigned formally to a metal-to-ligand charge transfer (MLCT)  $d_{x,z,yz}(\text{Co}^{\text{I}}) \rightarrow \pi^*(\text{pc})$  (refs<sup>41,50,51</sup>) and a shift to the red and decrease in intensity of the Q band. The UV-VIS spectrum of  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_4\text{pc}\}]^-$  is surprisingly similar to that<sup>40</sup> of  $[\text{Co}^{\text{I}}(\text{TNpc})]^-$  and is not red-shifted. In the spectrum of the corresponding complex  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}\}]^-$ , the MLCT band is clearly present and not red-shifted, but the Q band is so weak that it is hardly observable.

$\text{Co}^{\text{I}}\{\text{pc}(3-)\}^{2-}$ : The characteristic spectral change for the formation of  $\text{Co}^{\text{I}}\{\text{pc}(3-)\}^{2-}$  for  $[\text{Co}(\text{pc})]$  (refs<sup>38,40</sup>) and  $[\text{Co}(\text{Tspc})]$  (ref.<sup>21</sup>) species is a red-shift of the MLCT and Q-band transitions. Additional absorption bands in the NIR region are also observed. In these specific cases, the MLCT and Q bands are clearly separated and observed. However, as shown in Figs 4c and 4f, a broad multiple band is observed for these polynitro species. They are not so red-shifted as noted above for the copper and zinc analogues. Further reduction of  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_4\text{pc}(3-)\}^{2-}$  results in decomposition.

$[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(4-)\}^{3-}$  and  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(5-)\}^{4-}$ : Figures 4g and 4h show the spectral changes during the formation of  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(4-)\}^{3-}$  and  $[\text{Co}^{\text{I}}\{(\text{NO}_2)_8\text{pc}(5-)\}^{4-}$ . The UV-VIS spectra of the latter reduced species are very similar to those of  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(4-)\}^{2-}$  and  $[\text{Zn}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(5-)\}^{3-}$ , respectively, and, compared to the starting pc(3-)-complexes, are substantially red-shifted.

### Comparative Electrochemical Data

Table I compares the electrochemical data for the species under discussion together with some relevant literature data. The trends are as one would expect. All the redox processes shift to more positive values with the increasing number of acceptor substituents in the phthalocyanine ring. Thus, the Co(III)/Co(II) couple shifts from 0.38 V vs SCE in  $[\text{Co}^{\text{II}}(\text{TNpc})]$  to 0.82 V in the octanitrophthalocyanine species, a net shift of 0.5 V. The shift is more dramatic for the Co(II)/Co(I) couple where the octanitrophthalocyanine

species potential is some 0.76 V more positive than for [Co(TNpc)]. For ring-localized processes, the relative shift is even larger, being some 0.91 V for the  $\text{Co}^{\text{I}}\{\text{pc}(2-)\}/\text{Co}^{\text{I}}\{\text{pc}(3-)\}$  process (Table I). In the zinc phthalocyanine electrochemistry described in Table I, there is also a shift of 1 V or more, to more positive potential for ring-reduction processes, comparing [Zn(TNpc)] with [Zn{(NO<sub>2</sub>)<sub>8</sub>pc}]. Thus, the introduction of nitro groups in the phthalocyanine periphery has a dramatic effect in stabilizing vacant acceptor orbitals in the Mpc framework. Indeed, these [M<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}] species are very easily reduced: even traces of reducing impurities in a solvent reduce them. For example, dissolution of the [Co<sup>II</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}] complex in DMF under ambient conditions leads directly to [Co<sup>I</sup>{(NO<sub>2</sub>)<sub>8</sub>pc}]<sup>-</sup>, as demonstrated by its electronic spectrum, which is caused, no doubt, by the presence of trace dimethylamine as a reducing agent.

### Hammett Substituent Constants

Several studies have shown that the solution phase redox potentials of various processes involving substituted phthalocyanine derivatives, [M(R<sub>x</sub>pc)], correlate with the sum of the Hammett substituent constants<sup>6</sup>,  $\sigma_p$  (refs<sup>6,7,18,52-54</sup>), with slopes in the range 0.1–0.15 V/ $\sigma_p$ . The experimental data reported here can extend the previous database to and improve the statistics. The agreement with the previous correlation is excellent; the improved data are shown in Table III.

TABLE III

Correlation of redox potentials of ring-substituted phthalocyanine (pc) complexes in organic solvents<sup>a</sup> (V vs SCE) with Hammett substituent constant  $\sigma_p$

Redox process	Slope	Intercept	R <sup>b</sup>	Number <sup>c</sup>
$\text{Zn}^{\text{II}}\{\text{pc}(2-)\}/\text{Zn}^{\text{II}}\{\text{pc}(3-)\}^-$	0.12	-0.85	0.978	8
$\text{Zn}^{\text{II}}\{\text{pc}(3-)\}^-/\text{Zn}^{\text{II}}\{\text{pc}(4-)\}^{2-}$	0.14	-1.25	0.971	8
$\text{Cu}^{\text{II}}\{\text{pc}(2-)\}/\text{Cu}^{\text{II}}\{\text{pc}(3-)\}^-^d$	0.12	-0.77	0.978	8
$\text{Cu}^{\text{II}}\{\text{pc}(3-)\}^-/\text{Cu}^{\text{II}}\{\text{pc}(4-)\}^{2-}$	0.08	-1.17	0.947	8
$\text{Co}^{\text{II}}(\text{pc})/[\text{Co}^{\text{I}}(\text{pc})]^-$	0.15	-0.64	0.974	6
$\text{Co}^{\text{III}}(\text{pc})^+/\text{Co}^{\text{II}}(\text{pc})$	0.05	0.49	0.950	5

<sup>a</sup> Some data taken from refs<sup>7,16</sup>, new data are added. <sup>b</sup> Regression coefficient. <sup>c</sup> Number of observations. <sup>d</sup> Subject to uncertainty as to the identity of the 1e-reduced [Cu{(NO<sub>2</sub>)<sub>8</sub>pc}]<sup>-</sup> species.

Summarizing, electrochemical and spectroscopic properties of  $[\text{M}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  (M = Co, Cu and Zn) complexes were studied. The introduction of the strong  $\pi$ -acceptor nitro group in the phthalocyanine ring shifts the redox potentials dramatically to more positive values. Optical spectra are reported for a majority of the accessible oxidized and reduced species. Some variations from previously reported spectroscopic data are noted. The first reduced product of  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}\}]$  may be  $[\text{Cu}^{\text{I}}\{(\text{NO}_2)_8\text{pc}\}]^-$  and not  $[\text{Cu}^{\text{II}}\{(\text{NO}_2)_8\text{pc}(3^-)\}]^-$ .

We thank Ms P. Seymour, Dr M. N. Golovin and Prof. E. A. Lukyanets for technical help, and the Natural Sciences and Engineering Research Council, Ottawa, Canada, for financial support.

### REFERENCES AND NOTES

1. Lever A. B. P.: *CHEMTECH* **1987**, 506.
2. Leznoff C. C., Lever A. B. P. (Eds): *Phthalocyanines: Properties and Applications*, Vol. 1–4. John Wiley/VCH, New York 1989–1993.
3. McKeown N.: *Phthalocyanine Materials, Synthesis, Structure and Function*. CUP, Cambridge (U.K.) 1998.
4. Lever A. B. P.: *J. Porphyrins Phthalocyanines* **1999**, *3*, 488.
5. Lever A. B. P.: *Inorg. Chem.* **1990**, *29*, 1271.
6. Leo C., Hansch A., Taft R. W.: *Chem. Rev. (Washington D. C.)* **1991**, *91*, 165.
7. Lever A. B. P.: *Inorg. Chim. Acta* **1993**, *203*, 171.
8. Bazanov M. I., Shishkina O. V., Maizlish V. E., Petrov A. V., Shaposhnikov G. P., Smirnov R. P., Gzheidzyak A.: *Russ. J. Electrochem.* **1998**, *34*, 818.
9. Liu W., Xu Y., Ding Z.: *Gaodeng Xuexiao Huaxue Xuebao* **1992**, *13*, 254; *Chem. Abstr.* **1992**, *117*, 99542.
10. Wu X., Hu X.: *Wuji Huaxue* **1987**, *3*, 117; *Chem. Abstr.* **1987**, *108*, 15178.
11. Yang T., Zhuang R. F.: *Wuji Huaxue Xuebao* **1992**, *8*, 358; *Chem. Abstr.* **1994**, *120*, 146961
12. Achar B. N., Bhandari J. M.: *Transition Met. Chem. (London)* **1993**, *18*, 423.
13. Achar B. N., Bhandari J. M.: *Synth. React. Inorg. Met.-Org. Chem.* **1993**, *23*, 133.
14. Negrimovskii V. M., Derkacheva V. M., Kaliya O. L., Lukyanets E. A.: *Zh. Obshch. Khim.* **1991**, *61*, 460.
15. Negrimovskii V. M., Derkacheva V. M., Lukyanets E. A.: *Zh. Obshch. Khim.* **1989**, *59*, 1688.
16. Lever A. B. P., Milaeva E., Speier G. in: Ref.<sup>2</sup>, Vol. 3, p. 1. VCH, New York 1993.
17. Krejčík M., Daněk M., Hartl F.: *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *317*, 179.
18. Orihashi Y., Nishikawa M., Ohno H., Tsuchida E., Matsuda H., Nakanishi H., Kato M.: *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3731.
19. The standard oxidation state of the phthalocyanine unit is the dianion, formally pc(2-) but which for simplicity we write as pc. For clarity, the first oxidized state is written pc(1-) and the reduced states are consecutively pc(3-)...pc(6-).

20. Lever A. B. P., Hempstead M. R., Leznoff C. C., Liu W., Melnik M., Nevin W. A., Seymour P.: *Pure Appl. Chem.* **1986**, 58, 1467.
21. Nevin W. A., Liu W., Greenberg S., Hempstead M. R., Marcuccio S. M., Melnik M., Leznoff C. C., Lever A. B. P.: *Inorg. Chem.* **1987**, 26, 891.
22. Martin P. C., Gouterman M., Pepich B. V., Renzoni G. E., Schindele D. C.: *Inorg. Chem.* **1991**, 30, 3305.
23. Schutte W. J., Sluytersrehabach M., Sluyters J. H.: *J. Phys. Chem.* **1993**, 97, 6069.
24. Duro J. A., Torres T.: *Chem. Ber.* **1993**, 126, 269.
25. Yang Y. C., Ward J. R., Seiders R. P.: *Inorg. Chem.* **1985**, 24, 1765.
26. Kobayashi N., Lever A. B. P.: *J. Am. Chem. Soc.* **1987**, 109, 7433.
27. Blagrove R. J.: *Aust. J. Chem.* **1972**, 25, 2533.
28. Blower M. A., Bryce M. R., Devonport W.: *Adv. Mater.* **1996**, 8, 63.
29. Matsuzawa Y., Seki T., Ichimura K.: *Thin Solid Films* **1997**, 301, 162.
30. Giraudeau A., Louati A., Gross M., Andre J. J., Simon J., Su C. H., Kadish K. M.: *J. Am. Chem. Soc.* **1983**, 105, 2917.
31. Lukyanets E. A.: *Catalog of Electronic Spectra of Phthalocyanines, and Related Compounds*. Moscow Scientific Manufacturing Union, Division of the Scientific Research Institute for Technoeconomic Research, Moscow 1989.
32. Stillman M. J., Nyokong T. in: Ref.<sup>2</sup>, Vol. 1, p. 133. VCH, New York 1989.
33. Kobayashi N. in: Ref.<sup>2</sup>, Vol. 2., p. 97. VCH, New York 1993.
34. Mack J., Kirkby S., Ough E. A., Stillman M. J.: *Inorg. Chem.* **1992**, 31, 1717.
35. Mack J., Stillman M. J.: *Inorg. Chem.* **1997**, 36, 413.
36. Jin Z., Nolan K., McArthur C. R., Lever A. B. P., Leznoff C. C.: *J. Organomet. Chem.* **1994**, 468, 205.
37. Stillman M. J. in: Ref.<sup>2</sup>, Vol. 3, p. 227. VCH, New York 1993.
38. Clack D. W., Yandle J. R.: *Inorg. Chem.* **1972**, 11, 1738.
39. Dodd E. J., Hush N. S.: *J. Chem. Soc.* **1964**, 4607.
40. Nevin W. A., Hempstead M. R., Liu W., Leznoff C. C., Lever A. B. P.: *Inorg. Chem.* **1987**, 26, 570.
41. Minor P. C., Gouterman M., Lever A. B. P.: *Inorg. Chem.* **1985**, 24, 1894.
42. Cory M. G., Hirose H., Zerner M. C.: *Inorg. Chem.* **1995**, 34, 2969.
43. Golovin M. N., Seymour P., Jayaraj K., Fu Y. S., Lever A. B. P.: *Inorg. Chem.* **1990**, 29, 1719.
44. Louati A., El Meray M., Andre J. J., Simon J., Kadish K. M., Gross M., Giraudeau A.: *Inorg. Chem.* **1985**, 24, 1175.
45. Linder R. E., Rowland N. S., Hush N. S.: *Mol. Phys.* **1971**, 21, 417.
46. Rollmann L. D., Iwamoto R. T.: *J. Am. Chem. Soc.* **1968**, 90, 1455.
47. a) Schumann B., Woehrle D., Jaeger N. I.: *J. Electrochem. Soc.* **1985**, 132, 2144;  
b) Takeshita K., Ashida M.: *J. Electrochem. Soc.* **1992**, 139, 285.
48. Bernstein P. A., Lever A. B. P.: *Inorg. Chim. Acta* **1992**, 200, 543.
49. Homborg H., Kalz W.: *Z. Naturforsch., B: Chem. Sci.* **1984**, 39, 1490.
50. Stillman M. J., Thompson A. J.: *J. Chem. Soc., Faraday Trans. 2* **1974**, 70, 790.
51. Stillman M. J., Thompson A. J.: *J. Chem. Soc., Faraday Trans. 2* **1974**, 70, 805.
52. Gavrilov V. I., Tomilova L. G., Derkacheva V. M., Chernykh E. V., Shelepin I. V., Lukyanets E. A.: *Zh. Obshch. Khim.* **1983**, 53, 1347.
53. Gavrilov V. I., Konstantinov A. P., Derkacheva V. M., Lukyanets E. A., Shelepin I. V.: *Zh. Fiz. Khim.* **1986**, 60, 1448.



54. Ho W., Pietro W. J.: Unpublished results.
55. Manivannan V., Nevin W. A., Leznoff C. C., Lever A. B. P.: *J. Coord. Chem.* **1988**, *19*, 139.