# Protonation of cobalt tetraneopentoxyphthalocyanine as a function of oxidation state

Paul A. Bernstein and A. B. P. Lever*

*York University, North York, Ont., M3J 1P3 (Canada)*

### Abstract

The protonation of cobalt tetraneopentoxyphthalocyanine (CoTNPc) has been studied as a function of the oxidation state of this species. Data are reported for phthalocyanine cobalt(I), cobalt(II), cobalt(III) and cobalt(III) cation radical species, usually dissolved in dichlorobenzene (DCB). Upto four stepwise protonation processes were observed using trifluoroacetic (TFAA), hydrochloric or sulfuric acid. These were followed by recording the electronic spectra of these species as a function of acid concentration. Analysis of these spectra, which usually displayed isosbestic points, yielded stoichiometry and stability constant data and allowed for the identification of the spectra of the species generated. The spectra are discussed in terms of a previously reported model for protonation of phthalocyanine species. Electronic spectroscopic data are reported for protonated phthalocyanine radical species, for the first time. The basicity of these species decreases from the cobalt(I) species to the cobalt(III) radical cation species, in order of increasing oxidation state.

## Introduction

Phthalocyanines (MPc) have a wide variety of current and potential applications in many fields including dyestuff and pigments, photoconductive surfaces, electro- and photocatalysis, electrochromism, photodynamic therapy (cancer treatment), molecular metals etc. [1]. The presence of lone pairs on the peripheral bridging nitrogen atoms allows for these species to be protonated with from one to four protons being bound; such protonated species may well have special roles to play in these many applications since they affect both the overall charge and the redox characteristics of the species.

There have been many publications [2–17] reporting studies of such protonation as a function of a metal centre [5, 6, 7, 10, 11, 14], or with a common metal ion and as a function of a peripheral ring substituent [8, 9].

Protonated MPc species, formed by reaction with a general acid HA, exist as simple cations or may be stabilized [11] by ion pair formation with $HA_2^-$, by axial binding of anion A [8, 11] and by intramolecular hydrogen bonding to appropriate hydrogen bond acceptor substituents in the 3-position of the peripheral benzene ring [11].

It is apparently a frequent occurrence that an MPc species will take up two protons in one step yet provide evidence (*vide infra*) that only one of these protons is bound to the phthalocyanine unit [6, 8, 9, 11]. This is interpreted in terms of the formation of, for example $[MPc \cdot H^+]^+[HA_2]^-$. Evidence for this follows from the spectroscopic features of the molecule so formed, and also, where observed, the spectroscopic features of the next protonation step.

There does not appear to have been a systematic study of the spectroscopic features of protonation as a function both of the number of protons and the oxidation state of the central ion, nor a study of the variation of base strength of a MPc species as a function of oxidation state. Such a study is reported here for cobalt tetraneopentoxyphthalocyanine (CoTNPc) in four different oxidation states (defined here by the charge on the phthalocyanine unit, and oxidation state of the central cobalt ion, see ref. 18).

## Experimental

### Complexes

Cobalt 2,9,16,23-tetraneopentoxyphthalocyanine was prepared as $Co^{II}TNPc(-2)$ by the method published by Leznoff *et al.* [19]. Although a specific isomer is annotated here, in fact, the synthesis gives a mixture

---

*Author to whom correspondence should be addressed.

of isomers with neopentoxy groups randomly distributed (one per peripheral benzene ring) around the 4,5-positions of the phthalocyanine unit. The various isomers have essentially identical electronic spectra and are expected to have indistinguishable base strengths.

All the CoTNPc species to be discussed here, in their various oxidation states, have been characterized previously in unprotonated forms. Methods of preparation are summarized in refs. 20 and 21.

TBA[Co$^I$TNPc(−2)] was prepared by bulk electrolysis (−1.00 V versus AgCl/Ag, under N$_2$) of a $1 \times 10^{-4}$ M Co$^{II}$TNPc(−2) solution in 1,2-dichlorobenzene (DCB, Aldrich, Gold Label, dried over 4 Å molecular sieves) containing the electrolyte tetrabutylammonium hexafluorophosphate (0.07 M) (TBAPF$_6$, Aldrich, 98%, recrystallized from absolute ethanol (Consolidated Alcohols Ltd.), and dried at 140 °C for 2 h under vacuum (10$^{-3}$ torr)).

TBA[Cl$_2$Co$^{III}$TNPc(−2)] was prepared by bulk electrolysis (+0.90 V versus AgCl/Ag, under N$_2$) of a Co$^{II}$TNPc(−2)/DCB solution ($1.16 \times 10^{-4}$ M) containing 0.10 M tetrabutylammonium chloride (TBACl, Eastman, dried using 4 Å molecular sieves as an 0.10 M solution in DCB). The [Cl$_2$Co$^{III}$TNPc(−2)]$^-$ anion could also be chemically prepared either by adding microlitre quantities of concentrated aqueous HCl to Co$^{II}$TNPc(−2) ($1 \times 10^{-4}$ M) in dimethylformamide (1.00 ml) (DMF, Aldrich, 99+%, anhydrous, in an Aldrich Sure/Seal bottle), or by adding thionyl chloride (1 $\mu$l) (SOCl$_2$, BDH, reagent grade, sp. gr. = 1.64, nitrogen was bubbled through the SOCl$_2$ for 4 h, prior to use, to displace the gaseous impurities HCl, SO$_2$ and O$_2$) to a solution of Co$^{II}$TNPc(−2) ($1 \times 10^{-4}$ M) in DCB (1.00 ml) containing TBACl (0.1 M). Nitrogen was bubbled through the solution for 1 h, to remove the excess HCl and any unreacted SOCl$_2$.

Solutions of Cl$_2$Co$^{III}$TNPc(−1) were prepared chemically by adding SOCl$_2$ ($1.3 \times 10^{-2}$ M) to a 10$^{-4}$ M solution of Co$^{II}$TNPc(−2) in DCB. Nitrogen was bubbled through the solution for 1 h to remove the excess SOCl$_2$ and any HCl that may have been present.

*Methods*

Electronic absorption spectra were recorded with a Guided Wave Inc. model 100-20 optical waveguide spectrum analyzer using a caliper fiber optic probe and a 0.100 or 0.200 cm quartz cell. In a typical experiment, microliter quantities of trifluoroacetic acid (TFAA, Aldrich, 99%, sp. gr. = 1.48) were added to a solution of CoTNPc (in one particular oxidation state, ≈1 × 10$^{-4}$ M) in dry DCB (1.00 ml). The compounds Co$^{II}$TNPc(−2), TBA[Cl$_2$Co$^{III}$TNPc(−2)] and Cl$_2$Co$^{III}$TNPc(−1) were also dissolved in neat concentrated sulfuric acid (BDH, analytical reagent) to obtain the electronic spectra of these species in a highly

acidic environment. Only in the case of Co$^{II}$TNPc(−2) was dry HCl used. The HCl was prepared *in situ* by reacting 'tetrabutylammonium perchlorate' (TBAP, Fluka, >98%, recrystallized from absolute ethanol and dried at 70 °C under vacuum (10$^{-3}$ torr) for 2 days) with SOCl$_2$. (The TBAP contained ethanol, the solvent of recrystallization. Thionyl chloride reacts with ethanol to produce CH$_3$CH$_2$Cl, SO$_2$ and HCl. By comparing the electronic spectrum of Co$^{II}$TNPc(−2) in DCB/ethanol/SOCl$_2$ with that of DCB/TBAP/SOCl$_2$ it was estimated that the TBAP contained 5% ethanol by weight.)

Two methods were used to deprotonate the protonated CoTNPc compounds. Method 1 involved bubbling nitrogen through the DCB/CoTNPc/TFAA solution to displace the TFAA. Method 2 involved adding a microliter quantity (two-fold excess based upon the concentration of acid) of base (triethylammine (Et$_3$N, Aldrich, 99%) or pyridine (ACS grade)).

Due to the oxygen sensitivity of [Co$^I$TNPc(−2)]$^-$, careful attempts were made to exclude oxygen from this species. The TFAA and Et$_3$N were deoxygenated by bubbling nitrogen for 4 h through a small test tube containing about 5 ml of the reagent. All transfers were made under a nitrogen atmosphere.

## Results and discussion

*Introduction*

We have previously identified the electronic spectroscopic features which characterize each oxidation state of CoTNPc [20, 21]. The several oxidation states of CoTNPc may be prepared by chemical or electrochemical oxidation or reduction, as indicated in 'Experimental', with their identity being assured by their characteristic electronic spectrum. Thus these aspects of the problem are assumed without further discussion.

The addition of acid (trifluoroacetic, TFAA, or hydrochloric, see 'Experimental') led to successive protonation which was invariably demonstrated by a stepwise red shift in the Q band absorption.

Suppose, for the moment, that each protonation step is sufficiently separated from the next, that there exists an acid concentration (or range thereof) where essentially only one protonated species is present in solution. Then the titration of a CoTNPc species with acid, will yield a series of spectra, each pair demonstrating a set of isosbestic points, and separated by a regime of acid addition where no significant change in spectrum takes place.

There is no a priori reason to suppose that this assumption is valid. However, experimentally, this does seem to be the situation for many of the species studied previously in the literature, e.g. see sets of spectra

containing isosbestic points, in the stepwise protonation of metal free phthalocyanine [4] and of copper [9] and gallium(III) tetra-t-butylphthalocyanines [10]. From appropriate data sets, values of the stability constants, $K_n$ (*vide infra*) may be extracted and then used to confirm that there are indeed regions of acid concentration where one species greatly predominates.

The point group symmetry of these species depends in a critical fashion upon the degree (and sites) of protonation. Thus the actual spectrum often provides a clear indication of the actual degree of protonation present, and provides a check of the above assumption.

In this study the protonated species were deprotonated to recover the original spectrum and hence demonstrate the absence of decomposition. In some examples, however, chemical reaction occurred to give another product cleanly.

## Structure of protonated phthalocyanines

IR spectroscopy has shown that the interaction between MPc films and gaseous acids such as HAc, HCl and HBr is a completely reversible reaction [15]. Discrete acetate ions can be observed in the IR spectrum showing that molecules of acetic acid dissociate on contact with MPc and give up their protons to the pigment molecule. The most likely place for the protons to reside is on the bridging peripheral (sometime called *meso*) nitrogen atoms of the phthalocyanine molecule [6, 7, 9, 10, 11, 17]. We note that porphyrins do not contain bridge nitrogen atoms and frequently exhibit a blue shift in their electronic spectra upon protonation [22, 23]. Up to four protonation steps might be readily observable, with the possibility to observe a fifth and sixth protonation (on the inner nitrogen atoms) being very small since aside from the low basicity of the central nitrogen lone pairs, the overall positive charge on the complex will be large.

## The electronic spectra of protonated metallophthalocyanine species

### Introduction

In unprotonated metallophthalocyanines of $D_{4h}$ symmetry, the Q band and Soret bands are $\pi-\pi^*$ transitions, $a_{1u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$, respectively (Fig. 1). The electronic spectra of protonated phthalocyanines usually show a strong splitting of the Q band, indicative of a lowering of the symmetry of the molecule in a fashion dependent upon the number of protons, as shown in Fig. 1 and previously discussed [24].

The addition of one, two or three protons yields derivatives of $C_{2v}$ or $D_{2h}$ symmetry. In these point groups, the $e_g$ orbital splits, and the number of possible absorption bands doubles. Upon addition of a fourth proton, however, the symmetry of the metallophthalocyanine returns to $D_{4h}$ and only one principle Q band is predicted in the electronic spectrum. Therefore the tetraprotonation step is generally easy to diagnose.

To understand the bathochromic shifts of the absorption peaks one needs to consider the effect of protonation on the energies of the phthalocyanine orbitals. The $a_{1u}$ orbital has nodal planes passing through the bridging atoms [24–26] so that azo-protonation, to a first approximation, does not influence the energy of this orbital [5, 24]. The $a_{2u}$ orbital has significant electron density upon the bridging nitrogen atoms [24] so that it is stabilized by an amount $\Delta_1$ on the introduction of each proton.

Upon monoprotonation, the symmetry of the molecule drops to $C_{2v}$ and the $e_g$ orbital splits into $b_1$ and $a_2$ orbitals. The $b_1$ orbital is stabilized by an amount $\Delta_2$ while the $a_2$ orbital, with nodes at the bridging nitrogen atoms [24] remains unchanged. In the *trans*-diprotonated case, the $b_{2g}$ orbital remains at approximately constant energy and the $b_{3g}$ is lowered by an amount $2\Delta_2$. In the *cis*-diprotonated case, both orbitals are lowered by an amount $\Delta_3$. Application of these principles led Solovev et al. [24] to construct the energy level diagram in Fig. 1.

This four-orbital model qualitatively predicts the observed red shifts of the Q band upon protonation. An interesting feature of this model is that the *cis*-diprotonated isomer is not expected to exhibit a splitting of the Q band. Since the electronic spectra of diprotonated phthalocyanines always show a large splitting of the Q band [2, 3, 5, 7, 10, 11, 13] the protons must reside on opposite bridging nitrogen atoms (*trans*) rather than at adjacent nitrogens (*cis*) to reduce electrostatic repulsion interactions.

In most cases, the observation of definitive steps in the titration, coupled with the observed electronic spectrum leaves little doubt as to the protonation step being studied. The Q band shifts to the red in a stepwise fashion to a degree summarized in Table 1 which shows the average shifts upon each protonation step, abstracted from the literature.

The literature data used to derive Table 1 refer to unsubstituted phthalocyanine and to t-butyl substituted MPc species. Such data should be appropriate for discussion of the species under consideration here. However, we note that for some other substituted species, especially tetra-(3-X) derivatives where X can hydrogen bond to the proton site, the shifts for the first protonation step can be much larger than those shown in Table 1, indeed as much as $2000$ cm$^{-1}$ (*vide infra*) [8, 9].

Further, the spectra of the individual protonated species are sufficiently shifted with respect to one
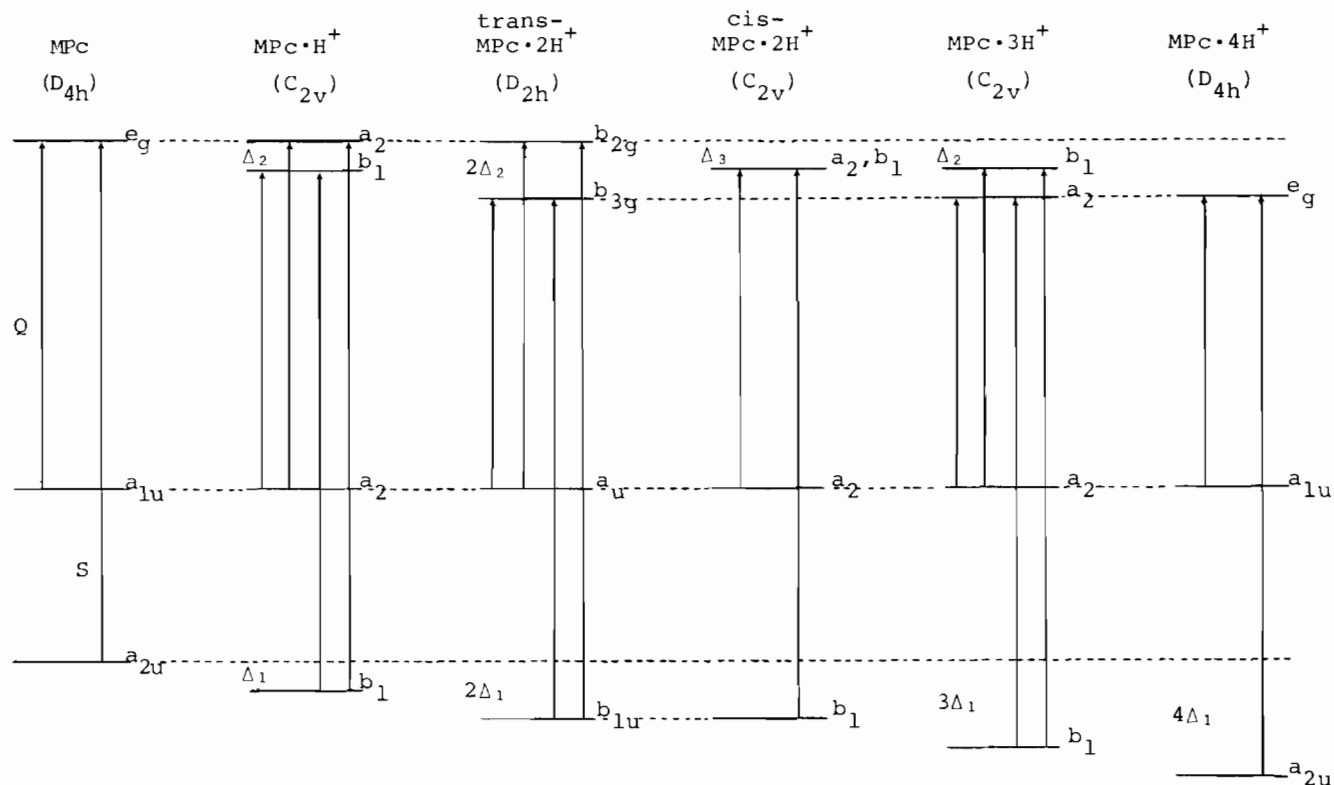
Fig. 1. Molecular orbital diagram showing the effect of protonation on the Q and Soret transitions.

TABLE 1. Summary of Q band shifts upon protonation[a]; data from the literature [2, 5, 7–11]

| Reaction | Number of examples | Average red shift[b] (cm$^{-1}$) |
|---|---|---|
| MPc + H$^+$ $\Longleftrightarrow$ MPc·H$^+$ | 16 | 700 ± 300 |
| MPc·H$^+$ + H$^+$ $\Longleftrightarrow$ MPc·2H$^+$ | 5 | 360 ± 50 |
| MPc·2H$^+$ + H$^+$ $\Longleftrightarrow$ MPc·3H$^+$ | 5 | 630 ± 60[c] |
| MPc·3H$^+$ + H$^+$ $\Longleftrightarrow$ MPc·4H$^+$ | 9 | 280 ± 70 |
| MPc + 2H$^+$ $\Longleftrightarrow$ MPc·2H$^+$ | 8 | 1050 ± 200 |
| MPc·2H$^+$ + 2H$^+$ $\Longleftrightarrow$ MPc·4H$^+$ | 2 | 460 ± 30 |

[a]Shift between the lowest energy Q band component of each species. This is by no means an exhaustive list, but is only used to provide a reasonable estimate of the shift expected for each protonation step. Specifically it is appropriate for unsubstituted or 4-alkyl substituted phthalocyanines (see text). [b]Relative shift for each protonation step. [c]The tetra(4-t-Bu)phthalocyanatogallium(III) species has a dramatically larger shift, c. 1300 cm$^{-1}$ at the third protonation step [10].

another that the contamination of one species by a few percent of a second species will often, though not always, be detectable through the presence of additional shoulders at wavelengths corresponding to the peak positions of the second species. We report here so-called limiting spectra (Table 2), which are believed to be primarily one species as identified on the basis of their stage of formation during the titration process, the observation of isosbestic points (and their subsequent shift), the lack of overlap with the spectra of adjacent species, and the detail of the spectra themselves (i.e. number of bands etc.). Where species exist in a wide range of acid concentration, spectra are reported for the maximum acid concentration which can be tolerated before new further protonated species begin to appear.

The analysis in Fig. 1 applies strictly to MPc($-2$) species of $D_{4h}$ symmetry. While a similar MO treatment can be applied to MPc($-3$) anion radicals and MPc($-1$) 'cation' radicals, the spectra to be expected will be quite different and have not been identified prior to this report. Such data are reported here, but their detailed analysis must await until a larger database of such species is available.

### Quantitative aspects

Stabilization of the excited state (by protonation) to a greater degree than the ground state will lower the energy of the electronic transition. Hence, a red shifting of the absorption bands indicates that phthalocyanines are stronger bases in the excited state than in the

TABLE 2. Electronic absorption maxima of protonated CoTNPc species

| Species[a] | Footnote | $\lambda$ (nm) ($\epsilon$, M$^{-1}$ cm$^{-1}$) | | Main Q band absorption | | |
|---|---|---|---|---|---|---|
| [Co$^I$TNPc($-2$)]$^-$ | b | 356sh | 472(38100) | 645(16800) | 710(54700) | |
| [Co$^I$TNPc($-2$)·H$^+$] | c | 413(13600) | | | 684(7940) | |
| [Co$^I$TNPc($-2$)·2H$^+$]$^+$ | d | 397(14100) | | 715sh | 766(43900) | |
| Co$^{II}$TNPc($-2$) | | 383(13800) | 614(24200) | | 680(83800) | |
| [Co$^{II}$TNPc($-2$)·H$^+$]$^+$ | e | 381(25900) | | | 700(48600) | |
| [Co$^{II}$TNPc($-2$)·2H$^+$]$^{2+}$ | f | 383(36300) | | 700(66900) | 733(94700) | |
| [Co$^{II}$TNPc($-2$)·3H$^+$]$^{3+}$ | g | 403(28500) | | 685(30700) | 729(48800) | 772(94300) |
| [Co$^{II}$TNPc($-2$)·4H$^+$]$^{4+}$ | h | 418(16500) | | 720sh | 815(81000) | |
| [Cl$_2$Co$^{III}$TNPc($-2$)]$^-$ | i | 369(30900) | 607(31800) | | 677(134000) | |
| [Cl$_2$Co$^{III}$TNPc($-2$)·2H$^+$]$^+$ | j | 384(38300) | 637sh | 702(64100) | 733(83100) | |
| [Cl$_2$Co$^{III}$TNPc($-2$)·4H$^+$]$^{3+}$ | | 413(27700) | 510(10900) | 686(20800) | 779(69800) | |
| Cl$_2$Co$^{III}$TNPc(1$-$) | l | 399(27100) | 540(29000) | 679sh | 755(22500)br | |
| [Cl$_2$Co$^{III}$TNPc(1$-$)·H$^+$]$^+$ | m | 409(24500) | 534(18600) | | 754(19500) | |
| [Cl$_2$Co$^{III}$TNPc(1$-$)·2H$^+$]$^{2+}$ | n | 404(21200) | | 688sh 743(26500) | 784(39400) | |
| [Cl$_2$Cl$^{III}$TNPc(1$-$)·4H$^+$]$^{4+}$ | h | 432br(18100) | 506br(17000) | 733sh 832(67100) | | |

[a][CoTNPc] $\approx 10^{-4}$ M in DCB solution, br = broad and sh = shoulder.  [b]Electrochemical reduction of Co$^{II}$TNPc($-2$)[TBAPF$_6$] = 0.048 M.  [c]With $2.6 \times 10^{-3}$ M TFAA and 0.094 M TBAP.  [d]With 0.55 M TFAA and 0.094 M TBAP.  [e][HCl] = $2.8 \times 10^{-4}$ M.  [f]With 0.100 M TBAP and 0.010 M HCl.  [g]With 0.100 M TBAP and 0.40 M HCl.  [h]In concentrated H$_2$SO$_4$.  [i]Electrochemical oxidation of Co$^{II}$TNPc($-2$) [TBACl] = 0.10 M.  [j]With 0.023 M TFAA and 0.018 M TBACl.  [k]With 0.32 M TFAA and 0.017 M TBACl.  [l]From the oxidation of Co(II)TNPc($-2$) with 0.013 M SOCl$_2$ (HCl-free).  [m]With 0.060 M TFAA.  [n]With 0.76 M TFAA.

ground state [27–30]. It is possible to estimate the excited state p$K_a$* (Table 3) using eqn. (1)

$$pK^* = pK + (0.625/T)(E(BH^+) - E(B)) \qquad (1)$$

where $E(BH^+)$ and $E(B)$ are the (0″–0′) transition energies in cm$^{-1}$ of the protonated and unprotonated species, respectively [28]. The p$K_a$* values obtained in this fashion though not usually very accurate [30] do provide a rough estimate of the true values.

Estimation of the excited state p$K_a$* has the advantage that only a shift of spectrum, upon protonation, need be measured, and the source and concentration of the proton source is irrelevant.

To estimate ground state p$K_a$ values, however, either the true pH must be known, or reliable acidity functions must be used. Since MPc protonation equilibria are rarely studied in water, but in organic solvents, pH values are generally not available. Most authors have

TABLE 3. Summary of reactions observed for TFAA protonation of CoTNPc in DCB (except where stated otherwise)

| Reaction | $n$[a] | $K$[a] | $K$*[b] |
|---|---|---|---|
| [Co$^I$Pc($-2$)]$^-$ + H$^+$ ⇔ Co$^I$Pc($-2$)·H$^+$ | 1[c] | $5.0 \times 10^{6c}$ | $3.7 \times 10^5$ |
| Co$^I$Pc($-2$)·H$^+$ + H$^+$ ⇔ [Co$^I$Pc($-2$)·2H$^+$]$^+$ | 1.2 | 4 | 8000 |
| Co$^{II}$Pc($-2$) + H$^+$ ⇔ [Co$^{II}$Pc($-2$)·H$^+$]$^+$ | 1.1 | 1000 | 8000 |
| [Co$^{II}$Pc($-2$)·H$^+$]$^+$ + H$^+$ ⇔ [Co$^{II}$Pc($-2$)·2H$^+$]$^{2+}$ | | | |
| [Co$^{II}$Pc($-2$)·2H$^+$]$^{2+}$ + H$^+$ ⇔ [Co$^{II}$Pc($-2$)·3H$^+$]$^{3+d}$ | 1.2 | 50 | 1500 |
| Co$^{II}$Pc($-2$) + H$_2$SO$_4$ ⇔ [Co$^{II}$Pc($-2$)·4H$^+$]$^{4+e}$ | | | |
| [Cl$_2$Co$^{III}$Pc($-2$)]$^-$ + 2H$^+$ ⇔ [Cl$_2$Co$^{III}$Pc($-2$)·2H$^+$]$^+$ | 1.8 | $10^{4f}$ | $2 \times 10^6$ |
| [Cl$_2$Co$^{III}$Pc($-2$)·2H$^+$]$^+$ + 2H$^+$ ⇔ [Cl$_2$Co$^{III}$Pc($-2$)·4H$^+$]$^{3+}$ | 1.7 | 900[f] | $5 \times 10^4$ |
| Cl$_2$Co$^{III}$Pc($-1$) + H$^+$ ⇔ [Cl$_2$Co$^{III}$Pc($-1$)·H$^+$]$^+$ | 1.0 | 60 | 60 |
| [Cl$_2$Co$^{III}$Pc($-1$)·H$^+$]$^+$ + H$^+$ ⇔ [Cl$_2$Co$^{III}$Pc($-1$)·2H$^+$]$^{2+}$ | 1.1 | 2 | 20 |
| Cl$_2$Co$^{III}$Pc($-1$) + H$_2$SO$_4$ ⇔ [Cl$_2$Co$^{III}$Pc($-1$)·4H$^+$]$^{4+e}$ | | | |

[a]Calculated using the Iodko method (eqns. (2)–(4)). Values of $K$ are only valid under the rather stringent conditions (DCB/TFAA) used in these experiments. The values cannot be readily transferred to a more classical aqueous phase acidity analysis.  [b]Calculated using eqn. (1) and $T = 295$ °K.  [c]For CoTNPc adsorbed on SAPG in 0.1 M phosphate buffer [36]. Note also comment in text that these protonated species may better be regarded as anion radical species of Co$^{II}$TNPc.  [d]Used TBAP, and SOCl$_2$ instead of TFAA.  [e]In concentrated H$_2$SO$_4$.  [f]$n$ was set equal to 2 for the evaluation of $K$.

used a range of different organic acids and reported equilibrium constants which are best regarded as stability constants for one or more protonation steps. Some acids, such as di- and trichloracetic acid are insufficiently strong to form tri- or tetraprotonated species, while others, specifically trifluoromethane sulfonic acid [10] (in trifluorobenzene solvent) and trifluoracetic acid (used here) often do permit up to four protonation steps to be observed. Strong mineral acids may also be employed to form tetraprotonated species, since MPc species are usually soluble and stable therein, at least at ambient temperature, for a significant period of time.

Some authors have employed well defined acidity functions [6, 7] but usually only for the weaker acidic conditions. For example, using acetic acid/sulfuric acid medium and buffered by antipyrin or urea [6], Al(III), Ga(III), In(III), Zr(IV) and Hf(IV) have $pK_a$ (first protonation step) values between 2 and 3, while OVPc and $H_2Pc$ are reported to have values near 0.7.

We were more interested in this study in comparing the behavior towards different oxidation states of the same metal phthalocyanine and have used common acidic conditions which lead to evaluation of comparable equilibrium or stability constants; however such equilibrium constants are not directly related to true thermodynamic $pK_a$ values without additional calibration and study, nor are they readily comparable to stability constants recorded with other acids or solvents, in the literature.

Following Iodko *et al.* [9, 11] the equilibrium constant, $K_n$ for the reaction

$$MPc + nH^+ \rightleftharpoons MPc \cdot nH^+ \qquad (2)$$
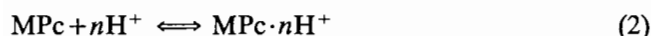
is given by

$$c_c/(c_0 - c_c) = Kc_{HA}{}^n \qquad (3)$$

where $c_{HA}$ is the concentration of the acid, assumed much larger than the initial concentration, $c_0$, of the MPc species, and where $c_c$, the concentration of the protonated species $[MPc \cdot nH^+]^{n+}$ can be determined from the absorbance of the solution, using

$$c_c = (D/b - \epsilon MPc\lambda c_0)/(\epsilon MPc \cdot nH\lambda - \epsilon MPc\lambda) \qquad (4)$$

where $b$ is the pathlength; $D$ is the optical density at wavelength, $\lambda$, at acid concentration $c_{HA}$; $\epsilon MPc\lambda$ is the extinction coefficient of MPc at wavelength $\lambda$, and $\epsilon MPc \cdot nH\lambda$ is the extinction coefficient of the protonated species obtained at a concentration $c_{HA}$ where the particular protonation step is complete.

By plotting the function of the left-hand side of eqn. (3) against $c_{HA}{}^n$, and varying $n$ to achieve a linear relationship [9, 11] the value of $n$, and of $K$, may be extracted.

On this basis there exists a fairly large body of data in the literature. Two conclusions are worth reporting here, for comparison with our new study.

Firstly, there is quite a range of basicity, as indicated by a large range in stability constant, from the most basic MPc species to the least, in the order [6]

$Sc(III) > Zn(II) > Al(III) >$

$In(III), Zr(IV), Hf(IV) > Ga(III) > Cu(II) >$

$H_2 > Pd(II) > OTi(IV) > OTa(IV) > ONb(IV) >$

$Si(IV) > Ge(IV) > Sn(IV) \qquad (5)$
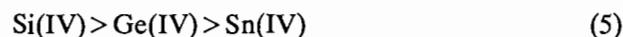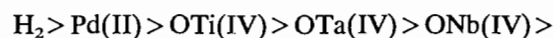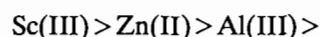
This order is rationalized superficially in terms of the degree of $\sigma$ and $\pi$ interaction between the central metal ion and the phthalocyanine ligand. Metal ions which form the most ionic bonds, at the left of the series, leave a larger net negative charge on the phthalocyanine unit and hence make it a better base.

In a study involving tetra-(3-X) and tetra-(4-X) substituted $H_2Pc$, CuPc and ZnPc [8, 9], wide variations were observed in $K_1$, the first protonation (or stability) constant for reaction with dichloracetic acid in nitrobenzene or 1-chloronaphthalene. The Q band shifts seen with these species were generally much greater than for the t-butyl substituted species, especially when a 3-X substituent could hydrogen bond to the proton. Moreover the red shift in the Q band was generally larger, the greater the magnitude of the stability constant, though no linear trends were observed. Thus increasing the basicity of the ground state by substitution (monitored by the magnitude of $K_1$) causes a concomitant larger basicity in the excited state (greater red shift).

This dual solvent study also revealed that the magnitude of $n$ (eqns. (2)–(4)) could, for the same species, be 1 in one solvent and 2 in the other, yet apparently have roughly the same electronic spectrum (as far as can be judged from tabulated data). This provides rather clear evidence that a value of $n = 2$ may be consistent with the binding of only one proton to the MPc unit, as originally suggested [11].

Finally we note that four protonation steps have been reported for $(HO)_2Si^{IV}TBuPc$ but that, from spectroscopic data, only three are attached to the peripheral nitrogen bridges [6].

*Spectroscopic data*

Using the above principles, it is now possible to discuss the protonated species involved in each oxidation state.

*Protonated $[Co^I TNPc(-2)]^-$ species.* Figure 2 shows the effect of adding TFAA to a solution of $[Co^I$-
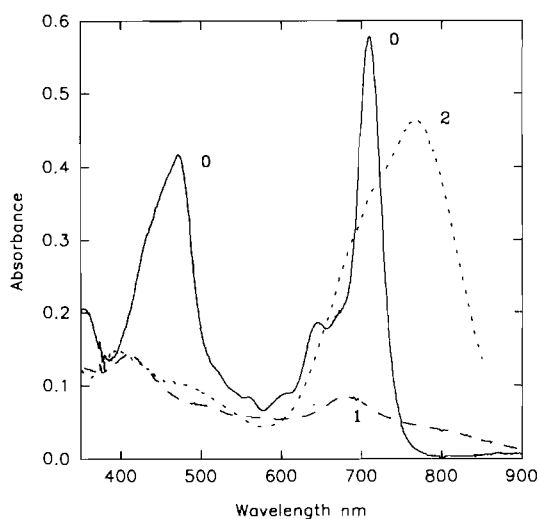
Fig. 2. Electronic absorption spectra of protonated [Co$^I$-TNPc(−2)]$^-$ species under nitrogen in DCB. [[Co$^I$-TNPc(−2)]$^-$]=1.06×10$^{-4}$ M and [TBAP]=0.094 M. 0, [Co$^I$-TNPc(−2)]$^-$, no acid present; 1, monoprotonated form Co$^I$TNPc(−2)·H$^+$ [TFAA]=0.0026 M; 2, diprotonated form [Co$^I$TNPc(−2)·2H$^+$]$^+$, [TFAA]=0.55 M.

TNPc(−2)]$^-$ in DCB. As titration proceeds there is a significant loss of the visible region absorption making it very difficult to identify the spectrum of a mono-protonated species. Further addition of acid, provides a recovery of the spectrum with growth of the Q band at 766 nm, corresponding to a shift of about 1000 cm$^{-1}$, from the Q band of the unprotonated species presumably to form the diprotonated form of [Co$^I$TNPc(−2)]$^-$. The addition of increasing amounts of TFAA to a solution of [Co$^I$TNPc(−2)·2H$^+$]$^+$ in DCB eventually caused a decrease (adjusted for the effect of dilution) in absorbance of the peak at 766 nm, indicating the formation of another protonated species. The electronic spectrum which showed maximum absorptivity at 766 nm was chosen as the final spectrum for [Co$^I$-TNPc(−2)·2H$^+$]$^+$. Isosbestic points were observed in the electronic spectra for the conversion of [Co$^I$-TNPc(−2)·H$^+$] to [Co$^I$TNPc(−2)·2H$^+$]$^+$, and analysis using the Iodko method showed $n=1$ (Table 3). However the absolute UV–Vis spectrum of the first protonated species is difficult to characterize because of the lack of strong absorption bands. It was logical, however, to assign the spectrum which showed the least absorption in the UV–Vis range and which showed no peaks, or significant shoulders, at 710 or 766 nm corresponding to contamination with unprotonated or diprotonated species respectively, as that for [Co$^I$-TNPc(−2)·H$^+$].

An attempt to obtain isosbestic points for the conversion of [Co$^I$TNPc(−2)]$^-$ to [Co$^I$TNPc(−2)·H$^+$] was

not made because of the sensitivity of the system towards oxygen.

The diprotonated species [Co$^I$TNPc(−2)·2H$^+$]$^+$, could be deprotonated back to the monoprotonated [Co$^I$TNPc(−2)·H$^+$] form simply by bubbling nitrogen through the solution for 20 min. Further bubbling to remove all traces of the TFAA, however, caused both deprotonation plus some oxidation likely from traces of oxygen in the nitrogen gas. Although the point was not proven, it is likely that the sensitivity of the Co$^I$TNPc species towards oxidation increases as the number of protons decreases (effect of net charge).

The addition of deoxygenated (by bubbling N$_2$) base (Et$_3$N, 0.18 M) also reversed the protonation of [Co$^I$TNPc(−2)·H$^+$], but again with contamination by Co$^{II}$TNPc(−2) products even when vacuum line or drybox techniques were used.

The spectroscopic behaviour upon titration with acid, and the Iodko analysis leave little doubt that the mono- and diprotonated species of [Co$^I$TNPc(−2)]$^-$ have been identified, but their spectra are anomalous (compare with those for Co$^{II}$TNPc in Fig. 3). The Q band signatures are unusual, and the monoprotonated species spectrum is exceptionally weak. Moreover, the band usually seen near 475–525 nm in [Co$^I$TNPc(−2)]$^-$ (see the unprotonated species spectrum in Fig. 2) and assigned to an MLCT transition [31] is absent from both protonated species.
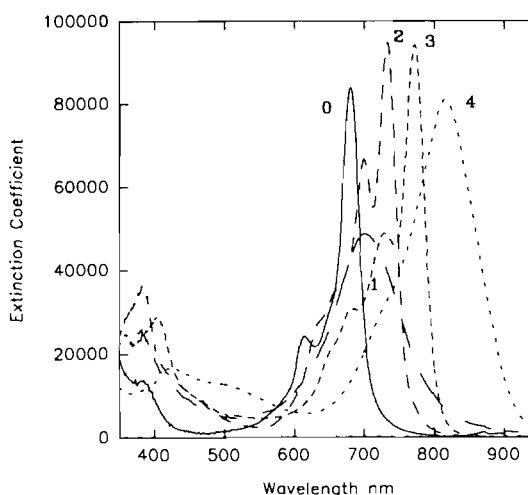


Fig. 3. Electronic spectra of protonated Co$^{II}$TNPc(−2) species. 0, [Co$^{II}$TNPc(−2)]=5.65×10$^{-5}$ M in DCB, no acid present; 1, monoprotonated form [Co$^{II}$TNPc(−2)·H$^+$]$^+$=1.33×10$^{-4}$ M in DCB [HCl]=2.8×10$^{-4}$ M; 2, diprotonated form [Co$^{II}$-TNPc(−2)·2H$^+$]$^{2+}$=9.40×10$^{-5}$ M in DCB [TBAP]=0.100 M, [HCl]=0.010 M; 3, triprotonated form [Co$^{II}$TNPc(−2)·3H$^+$]$^{3+}$=8.58×10$^{-5}$ M in DCB, [TBAP]=0.100 M, [HCl]=0.40 M; 4, tetraprotonated form [Co$^{II}$TNPc(−2)·4H$^+$]=4.52×10$^{-5}$ M in concentrated H$_2$SO$_4$.

Reduction of Co(II)R₄Pc(−2) species (R = various benzene ring substituents) invariably [20, 21, 32] yields [Co$^I$R₄Pc(−2)]$^-$, with reduction to [Co$^I$R₄Pc(−3)]$^{2-}$ occurring at potentials a volt or so more negative. Theoretically, however, one could conceive of forming [Co$^{II}$R₄Pc(−3)]$^-$ instead of [Co$^I$R₄Pc(−2)]$^-$. Protonation should stabilize the anion radical (Pc(−3)) form which will be a stronger base at the peripheral nitrogen atoms than will Pc(−2). Then the protonated first reduced species would be [Co$^{II}$TNPc(−3)·H$^+$] and the MLCT transition would be absent. While Pc(−3) species usually do yield absorption in the 500 nm region, due to $\pi^*$–$\pi^*$ transitions [33, 34] the spectra for protonated analogues are not known.

*Protonated Co$^{II}$TNPc(−2) species.* The titration of Co$^{II}$TNPc(−2) with acid yielded a clear stepwise process resulting in the formation of four discrete species as indicated by electronic spectroscopy (Figs. 3 and 4, Table 2). The first protonated Co$^{II}$TNPc(−2) species exhibited a broad, relatively weak peak at 700 nm. This is true of other monoprotonated phthalocyanine species [2, 5] and is probably an aggregation effect. The second and third protonated species showed strong splitting of the Q band as a result of the decrease in symmetry of the molecule. Isosbestic points were obtained (for example, Fig. 4) in the absorption spectra for the conversions from Co$^{II}$TNPc(−2) to [Co$^{II}$TNPc-(−2)·H$^+$]$^+$ to [Co$^{II}$TNPc(−2)·2H$^+$]$^{2+}$ to [Co$^{II}$TNPc-(−2)·3H$^+$]$^{3+}$.

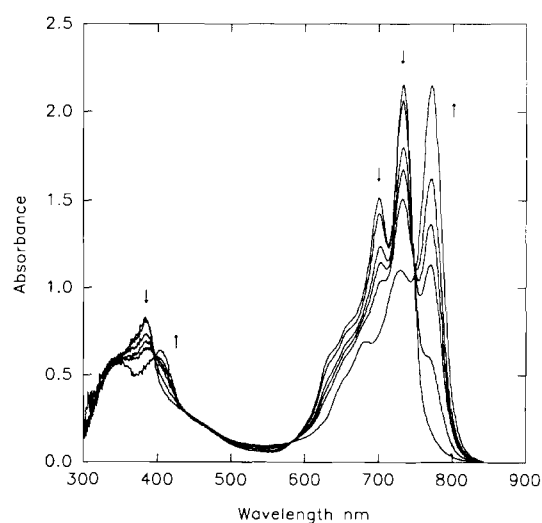Using the Iodko method [9, 11], $n$ and $K$ values were calculated for two of the above three protonation



Fig. 4. Electronic spectra showing the conversion of [Co$^{II}$-TNPc(−2)·2H$^+$]$^{2+}$ to [Co$^{II}$TNPc(−2)·3H$^+$]$^{3+}$ in DCB containing 0.0100 M TBAP, 1.13×10⁻⁴ M Co$^{II}$TNPc(−2) and HCl ([HCl] = 0.010 M, 0.030 M, 0.050 M, 0.060 M, 0.090 M and 0.40 M reading from the lower to the upper trace at 772 nm.).

reactions (Table 3). The number of protons, $n$, involved in each step was determined to be one. Values of $n$ and $K$ could not be determined for the middle process of [Co$^{II}$TNPc(−2)·H$^+$]$^+$ to [Co$^{II}$TNPc(−2)·2H$^+$]$^{2+}$ because of the relatively large number (3) of equilibria overlapping one another.

[Co$^{II}$TNPc(−2)·3H$^+$]$^{3+}$ can be prepared by dissolving Co$^{II}$TNPc(−2) in neat trifluoroacetic acid. It is identified through the similarity of its electronic spectrum to those of other triprotonated species in the literature [5, 7] and by its formation after two previous protonation steps.

In concentrated sulfuric acid, a fourth complex was obtained, assigned to [Co$^{II}$TNPc(−2)·4H$^+$]$^{4+}$ because its spectrum was similar to that of Co$^{II}$TNPc(−2), but broader and shifted to much longer wavelengths. The spectrum of [Co$^{II}$TNPc(−2)·4H$^+$]$^{4+}$ also resembled those of other tetraprotonated phthalocyanines reported in the literature [2–5, 10, 12]. The observation of only one strong Q band peak (at 815 nm) and a shoulder (probably a vibrational satellite) leads one to conclude that all four bridging nitrogen atoms are protonated and that the symmetry of the CoTNPc molecule has returned to $D_{4h}$.

The electronic spectra observed for all four species followed the predictions outlined above. Limiting spectra are shown in Fig. 3, where one may conclude that the triprotonated species is not contaminated by the tetraprotonated species, and the diprotonated species is not contaminated with the triprotonated species. They are further analyzed below.

[Co$^{II}$TNPc(−2)·nH$^+$]$^{n+}$ species ($n = 1$, 2 or 3) in DCB/ethanol could be deprotonated ($c$. 80% recovery, based on the height of the Q band of the Co$^{II}$TNPc(−2)) by adding aqueous NaOH. Bubbling nitrogen through a solution of [Co$^{II}$TNPc(−2)·3H$^+$]$^{3+}$ in DCB ([TFAA] = 0.32 M) to displace the acid, quantitatively reversed the protonation albeit slowly.

The addition of Et₃N to a solution of [Co$^{II}$-TNPc(−2)·3H$^+$]$^{3+}$ reversed the protonation, but the metallophthalocyanine was oxidized to [Co$^{III}$TNPc-(−2)]$^+$ (97% yield based on the electronic spectrum). Oxidation of Co$^{II}$TNPc(−2) to [Co$^{III}$TNPc(−2)]$^+$ also occurs when concentrated aqueous HCl is added to a solution of Co$^{II}$TNPc(−2) in DMF. In these experiments, oxygen is present and the oxidation product is [X₂Co$^{III}$TNPc(−2)]$^{n+}$ where X = Et₃N, DMF or Cl$^-$. The conversion to a Co$^{III}$Pc species is driven by the presence of a ligand (DMF, Et₃N or Cl$^-$) and the strong advantage of forming a six-coordinate, low-spin d⁶ Co$^{III}$ configuration [35]. If either the acid or a coordinating ligand is absent from the system, Co$^{III}$Pc species are not obtained.

*Protonated [Cl₂CoᴵᴵᴵTNPc(−2)]⁻ species.* Using TFAA, two protonated $[Cl_2Co^{III}TNPc(-2)]^-$ species were identified in DCB using UV–Vis spectroscopy (Fig. 5, Table 2). Isosbestic points were also obtained for the conversion of $[Cl_2Co^{III}TNPc(-2)]^-$ to the first protonated species and for the conversion of the first protonated species to the second protonated species.

The Iodko analysis yields $n = 2$ for the first protonation step. However the spectrum is inconsistent with that expected for a monoprotonated species. The shift of the Q band ($1130\ cm^{-1}$) upon protonation, and the striking resemblance to the spectrum of $[Co^{II}\text{-}TNPc(-2)\cdot2H^+]^{2+}$ (Fig. 3, Table 2) and other diprotonated species [2, 3, 5, 7, 10–12] indicates that *two* protons are bound to the 'first' protonated form of $[Cl_2Co^{III}TNPc(-2)]^-$. Thus in this case, $n = 2$, does not appear to be a consequence of ion pair formation with $[HA_2]^-$ (see discussion above).

Similarly, the shift of the Q band ($810\ cm^{-1}$) and the resemblance to other tetraprotonated species [2, 5, 10, 12] suggests that four protons are bound to the 'second' protonated $Cl_2Co^{III}TNPc(-2)$ species. The calculation of $n$ (Table 3) also confirms that two protons are involved in this process.

If the tetraprotonated spectrum had not appeared on the 'second' protonation step, then there would have been serious doubt about the first $n = 2$ step involving two, rather than one, protons attached to the MPc unit. The spectrum is supportive, but not definitive for a doubly protonated species. However the next step does appear to go directly to the tetraprotonated species. Thus these reactions appear to be genuine two-proton
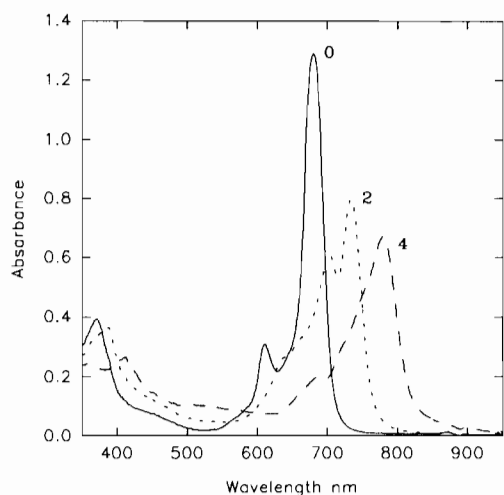


Fig. 5. Comparison of the electronic spectra of $[Cl_2Co^{III}TNPc(-2)]^-$, $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ and $[Cl_2Co^{III}TNPc(-2)\cdot4H^+]^{3+}$ in DCB containing $4.81\times10^{-5}$ M CoTNPc and 0.018 M TBACl. 0, $[Cl_2Co^{III}TNPc(-2)]^-$, no acid present; 2, diprotonated form [TFAA] = 0.023 M; 4, tetraprotonated species, [TFAA] = 0.32 M.

steps, clearly because, in each case, the second stability constant is larger than the first; the reason for this is not apparent.

The electronic spectrum which showed the maximum absorbance at 733 nm (the strongest peak characteristic of the first protonated species) was chosen as the limiting spectrum of $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$. This electronic spectrum (Fig. 5) did not exhibit shoulders at 677 nor 779 nm due to contamination with either unprotonated $[Cl_2Co^{III}TNPc(-2)]^-$ or $[Cl_2Co^{III}TNPc(-2)\cdot4H^+]^{3+}$, respectively.

A limiting spectrum of $[Cl_2Co^{III}TNPc(-2)\cdot4H^+]^{3+}$ could not be obtained directly by the addition of increasing amounts of TFAA to a solution of $[Cl_2Co^{III}TNPc(-2)]^-$ in DCB. At a concentration of TFAA of 0.32 M electronic spectroscopy revealed that $[Cl_2Co^{III}TNPc(-2)\cdot4H^+]^{3+}$ exists in admixture with $\approx10\%$ of $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ as indicated by a strong shoulder at 744 nm. Addition of more TFAA (0.56 M), however, resulted in the complete collapse of the absorption spectrum and inability to deprotonate the species cleanly with base. Dissolution of $[Cl_2Co^{III}TNPc(-2)]^-$ in concentrated $H_2SO_4$ also yields a weak electronic spectrum with evident decomposition. To obtain an estimate of the electronic spectrum of $[Cl_2Co^{III}TNPc(-2)\cdot4H^+]^{3+}$, the spectrum of $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ was subtracted from that of a spectrum of a mixture of the two species until the strong shoulder at 744 nm no longer appeared. The resulting spectrum of $[Cl_2Co^{III}TNPc(-2)\cdot4H^+]^{3+}$ is shown in Fig. 5.

Bubbling nitrogen through a solution of $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ in DCB/DMF (50:50 by volume [TFAA] = 2.4 M) reversed the protonation, but slowly. After two days of bubbling (to displace the TFAA) only 50% of the $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ had been deprotonated as indicated by electronic spectroscopy. The addition of base ($Et_3N$, 2.2 M) to this solution quantitatively reversed the protonation. The tetraprotonated species can also be reversed to unprotonated $Co^{III}$ species by reaction with $Et_3N$.

The striking similarity between the electronic spectra of $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ and $[Co^{II}\text{-}TNPc(-2)\cdot2H^+]^{2+}$ (see Figs. 4 and 5, Table 2) did prompt some concern that they were in fact the same species. However deprotonation of $[Cl_2Co^{III}TNPc(-2)\cdot2H^+]^+$ yields $[Cl_2Co^{III}TNPc(-2)]^-$ while deprotonation of $[Co^{II}TNPc(-2)\cdot2H^+]^{2+}$ yields $Co^{II}\text{-}TNPc(-2)$; thus these two diprotonated species are indeed different.

*Protonated $Cl_2Co^{III}TNPc(-1)$ species (cation radical species).* Using DCB and TFAA, two protonation products of $Cl_2Co^{III}TNPc(-1)$ were identified using UV–Vis spectroscopy. A third protonated form of

$Cl_2Co^{III}TNPc(-1)$ was observed in sulfuric acid (Fig. 6). Calculated values of $n$ (Table 3) indicate that the first protonated species in DCB is $[Cl_2Co^{III}TNPc(-1) \cdot H^+]^+$ and that the second is $[Cl_2Co^{III}TNPc(-1) \cdot 2H^+]^{2+}$. Isosbestic points were also obtained in the conversion of $Cl_2Co^{III}TNPc(-1)$ to $[Cl_2Co^{III}TNPc(-1) \cdot H^+]^+$ and $[Cl_2Co^{III}TNPc(-1) \cdot H^+]^+$ to $[Cl_2Co^{III}TNPc(-1) \cdot 2H^+]^{2+}$. The protonated species in concentrated sulfuric acid was assigned as $[Cl_2Co^{III}TNPc(-1) \cdot 4H^+]^{4+}$ due to the position and symmetrical nature of the Q band. The triprotonated species was not identified since dissolution in neat TFAA yielded the diprotonated species.
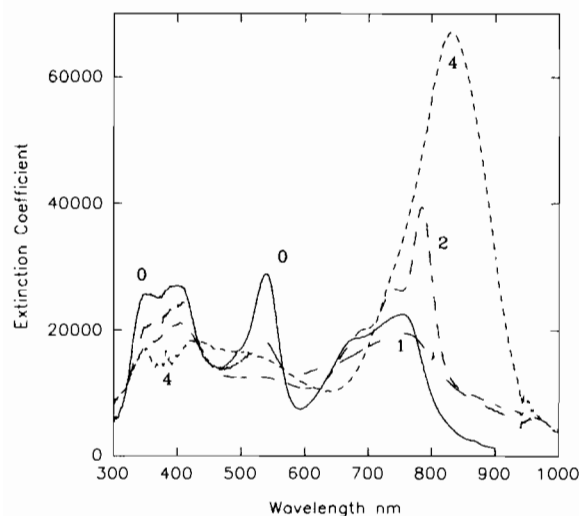


Fig. 6. Electronic spectra of protonated $Cl_2Co^{III}TNPc(-1)$ species in DCB. 0, $Cl_2Co^{III}TNPc(-1) = 8.62 \times 10^{-5}$ M, no acid present; 1, monoprotonated form $[Cl_2Co^{III}TNPc(-1) \cdot H^+]^+ = 7.50 \times 10^{-5}$ M, $[TFAA] = 0.11$ M; 2, diprotonated form $[Cl_2Co^{III}TNPc(-1) \cdot 2H^+]^{2+} = 1.86 \times 10^{-4}$ M, $[TFAA] = 0.76$ M; 4, tetraprotonated species $[Cl_2Co^{III}TNPc(-1) \cdot 4H^+]^{3+} = 1.19 \times 10^{-4}$ M in concentrated $H_2SO_4$.

TABLE 4. Amount of TFAA required to generate the first protonated form of a solution containing $[CoTNPc] = \approx 1 \times 10^{-4}$ M solution of CoTNPc in DCB

| Oxidation state | [TFAA] (M) | |
| --- | --- | --- |
| | Experimental | Calculated[a] |
| $[Co^{I}TNPc(-2)]^-$ | $\leq 0.0026$ | |
| $Co^{II}TNPc(-2)$ | 0.0078 | 0.0090 |
| $[Co^{III}TNPc(-2)]^+$ | 0.023–0.042[b] | 0.030[b] |
| $[Co^{III}TNPc(-1)]^{2+}$ | 0.060–0.14 | 0.15 |

[a]The equilibrium constant for the first protonation reaction (Table 3) was used to calculate the concentration of TFAA such that $[CoTNPc \cdot H^+] : [CoTNPc] = 9:1$. [b]Note, that the first protonated species is $[Co^{III}TNPc(2-) \cdot 2H^+]^{3+}$.

In common with other monoprotonated species, the spectrum of the first product, presumably $[Cl_2Co^{III}TNPc(-1) \cdot H^+]^+$ is rather broad. That it is a true monoprotonated species and not, in fact, a mixture of zero and diprotonated species appears unlikely since, in the Q band region, its absorbance is less than that of either of these species.

A solution of $[Cl_2Co^{III}TNPc(-1) \cdot 2H^+]^{2+}$ in DCB with 1.2 M TFAA could be completely converted to unprotonated $Cl_2Co^{III}TNPc(-1)$ by bubbling nitrogen through the solution for an hour. Addition of base (0.18 M $Et_3N$ or 1.1 M pyridine), however, to any $Cl_2Co^{III}TNPc(-1)$ solution (protonated or otherwise) resulted in the reduction of the $Cl_2Co^{III}TNPc(-1)$ to $Co^{II}TNPc(-2)$. A two-electron oxidation process appears to occur in this reaction which would bear further study.

## Effect of oxidation state on protonation

Four different oxidation states of CoTNPc were used in this study differing from one another by the number of electrons and hence charge (neglecting axial ligands and counterions) on the CoTNPc moiety. There exists a clear relationship between the net charge on the CoTNPc unit (neglecting axial ligands) and the relative ease of protonation of the molecule.

As the positive charge on the cobalt phthalocyanine molecule increases, so does the amount of TFAA required to shift the equilibrium towards the first protonated form. Table 4 shows the approximate amount of TFAA needed to achieve the first protonation of a $1 \times 10^{-4}$ M solution of CoTNPc, in its different oxidation states, in DCB. This provides an immediate, fairly quantitative, measure of the relative basicities of the various oxidation states of CoTNPc. Not surprisingly, the basicity decreases with increasing net oxidation level of the species.

Other experiments have supported this trend. Oxidation of $[Co^{I}TNPc(-2) \cdot H^+]$ by molecular oxygen yields unprotonated $Co^{II}TNPc(-2)$. The pH dependence studies of the $Co^{II}/Co^{I}$ wave of CoTNPc adsorbed on a highly oriented pyrolytic graphite (HOPG) electrode were interpreted in terms of the $Co^{I}$ oxidation state being protonated and the $Co^{II}$ oxidation state being unprotonated [36].

Similarly thionyl chloride containing trace HCl impurity is known to oxidize $[Co^{II}TNPc(-2) \cdot H^+]^+$ to unprotonated $Cl_2Co^{III}TNPc(-1)$, and $[Cl_2Co^{III}TNPc(-2) \cdot 2H^+]^+$ to unprotonated $Cl_2Co^{III}TNPc(-1)$ [37, 38].

This effect is purely electronic in nature — the greater the positive charge on the phthalocyanine molecule, the more difficult it is to protonate. The presence of axial ligands on the central metal, as in the $Co^{III}TNPc$

species, appears to have little effect upon the basicity of the peripheral bridging nitrogen atoms, even though the overall charge may become negative. Unfortunately it is not possible to fit these cobalt species into the sequence of basicity (5).

Single proton, stepwise protonation was observed for all the species except $[Cl_2Co^{III}TNPc(-2)]^-$ which appears to simultaneously bind two protons forming a true diprotonated species, rather than a monoprotonated species ion paired with $[HA_2]^-$. There then follows a second two-proton step to a species whose electronic spectrum identifies it as the tetraprotonated species. Thus $[Cl_2Co^{III}TNPc(-2)]^-$ appears unique in participating in genuine two-proton steps.

### Comparison of spectroscopic data with theory

The overall appearance of the electronic spectra of the protonated CoTNPc species agree with the predictions discussed above and summarized in Fig. 1. Thus the number of Q band transitions follows as expected. Indeed all three tetraprotonated species recorded, have almost identical band shapes, though that for $Cl_2Co^{III}TNPc(-1)$ is remarkably strong (Fig. 6).

TABLE 5. Magnitude of $\Delta_2$ from analysis of spectroscopic data

| Complex[a] | Method[b] | Magnitude of $\Delta_2$ $(cm^{-1})^b$ | Reference |
|---|---|---|---|
| $[Co^ITNPc(-2)]^-$ | ii | 930 | this work |
| $Co^{II}TNPc(-2)$ | ii | 320 | this work |
| | iii | 765 | |
| | iv | 1215 | |
| $[Cl_2Co^{III}TNPc(-2)]^-$ | ii | 300 | this work |
| | iv | 970 | |
| $Cl_2Co^{III}TNPc(-1)$ | ii | 350 | this work |
| | iv | 600 | |
| $Zn^{II}Pc$ | i | 540 | 7 |
| | ii | 350 | |
| $Zn^{II}TBuPc$ | i | 600 | 8 |
| $Zn^{II}T(3-MeO)Pc$ | i | 670 | 8 |
| $(HO)_2Hf^{IV}Pc$ | i | 490 | 7 |
| $Ga^{III}TBuPc$ | i | 500 | 10 |
| | ii | 300 | |
| | iii | 1300 | |
| $Cu^{II}TBuPc$ | i | 580 | 11 |
| | ii | 350 | |

[a]The parent unprotonated species is listed. [b]The magnitude of $\Delta_2$ is derived using the model in Fig. 1. i: the splitting of the Q band of the monoprotonated species, ii: one-half the splitting observed for the Q bands of the diprotonated species, iii: equal to the splitting observed for the triprotonated Q band absorption, iv: one-half the shift between the Q band of the tetraprotonated and unprotonated species.

Three of the diprotonated species have very similar spectra, while the fourth, that of $[Co^ITNPc(-2)]^-$ is anomalous perhaps for the reasons discussed above.

However one may also predict that, for example, in the trans-diprotonated species, one component of the Q band should be observed at essentially the same energy as in the unprotonated species (see Fig. 1). This is actually observed for the $[Co^ITNPc(-2)]^-$ species, but is less accurately true for the other species. Since the shifts are, however, quite small, the agreement is probably as good as one may expect.

Values for $\Delta_2$ may be extracted from the data in Table 2 in several fashions (see footnotes to Table 5). Probably the splitting in the Q bands for the trans-diprotonated and triprotonated species provide the most accurate assessment since they do not require the assumption that, when comparing pairs of complexes, one level, such as $a_2(e_g)$ in the monoprotonated species remains at the same level as the initial $e_g$ energy.

These data are summarized in Table 5 where they are compared with related data from the literature. There is no a priori reason why the value of $\Delta_2$ should be independent of the degree of protonation. Thus the variation seen in Table 5 should not be surprising. *Ab initio* calculations are planned to see if these splittings can be calculated accurately and hence determine the shifts in energy levels which give rise to them. However they are of such relatively small magnitude that a very accurate calculation would be needed if meaningful results are to be obtained. It would be useful if the magnitude of $\Delta_2$ were to be experimentally related to the magnitude of the stability constant, as might reasonably be inferred from the treatment summarized in Fig. 1. Regrettably however, even where closely related series of tetra-(3-X) and tetra-(4-X) substituted Zn, Cu, $H_2Pc$ are concerned [8, 9] the correlation between $K_1$ and $\Delta_2$, while suggestive (species with the largest $K_1$ do have the largest $\Delta_2$) is very badly scattered.

### Conclusions

Many protonated CoTNPc species have been characterized (Tables 2 and 3). In most cases, stepwise protonation was observed with the maximum number of protons being equal to four. For most of the CoTNPc species (all but the $[Co^ITNPc(-2)]^-$ series), the protonation reaction could be completely reversed by either bubbling nitrogen to displace the acid, or by the addition of base.

Large ($\approx 500$ cm$^{-1}$) bathochromic shifts of the CoTNPc Q band were observed in the electronic spectrum for each bound proton. In the case of Co$^{II}$-TNPc($-2$) and [Cl$_2$Co$^{III}$TNPc($-2$)]$^-$ a red shifting ($\approx 900$ cm$^{-1}$/proton) of the Soret peak in the near UV region was also observed, but, in general there were no well defined variations in Soret band energies, perhaps because of mixing with closely lying higher energy states.

Surprisingly, each oxidation state of CoTNPc showed different and unique behaviour. The different oxidation states of CoTNPc can be ordered as follows by increasing basicity

$$Cl_2Co^{III}TNPc(-1) < [Cl_2Co^{III}TNPc(-2)]^- <$$

$$Co^{II}TNPc(-2) < [Co^ITNPc(-2)]^- \qquad (6)$$
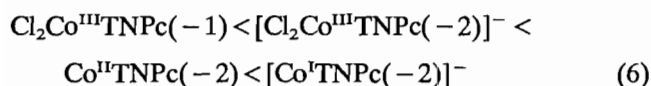
A clear trend has emerged — the lower the net oxidation state, the greater the basicity; evidently the overall charge, as dictated by the presence or absence of charged axial ligands, is largely unimportant.

There has only been one example of a protonated cobalt phthalocyanine species reported in the literature. Achar et al. [39] report the electronic spectrum (peaks at 738 and 388 nm) of cobalt tetraaminophthalocyanine (Co$^{II}$TAPc($-2$)) in 30 N H$_2$SO$_4$. This molecule, with four amine groups on the outer benzene rings is much more complicated with respect to protonation behaviour, than CoTNPc. In concentrated sulfuric acid one would expect all four amine substituents on CoTAPc to be protonated as well as some of the phthalocyanine bridge nitrogen atoms; the Q band energy is consistent with only 2 or 3 protons attached to the bridging nitrogen atoms.

This current work is the first study of protonated cobalt phthalocyanine species and the effect of oxidation state of a phthalocyanine compound on protonation, and the first reported data for protonation of a MPc($-1$) species.

## Acknowledgements

## References

1 A. B. P. Lever, Chemtech, 17 (1987) 506.
2 S. Gaspard, M. Verdaguer and R. Viovy, C. R. Acad. Sci. Paris, Series C, 277 (1973) 821.
3 S. Gaspard, M. Verdaguer and R. Viovy, J. Chim. Phys. Chim. Biol., 69 (1972) 1740.
4 S. Gaspard, M. Verdaguer and R. Viovy, J. Chem. Res. S, (1979) 271.
5 S. Gaspard and R. Viovy, J. Chim. Phys. Phys.-Chim. Biol., 78 (1981) 851.
6 A. S. Akopov and Yu. N. Borovkov, Koord. Khim., 14 (1988) 731.
7 Yu. N. Borovkov and A. S. Akopov, Zh. Fiz. Khim., 60 (1986) 750.
8 V. M. Derkacheva, O. L. Kaliya and E. A. Luk'yanets, Zh. Obshch. Khim., 53 (1983) 188.
9 V. M. Derkacheva, S. S. Iodko, O. L. Kaliya and E. A. Luk'yanets, Zh. Obshch. Khim., 51 (1981) 2319.
10 S. S. Iodko, O. L. Kaliya, N. V. Kondratenko, E. A. Luk'yanets, V. I. Popov and L. M. Yagupol'skii, Zh. Obshch. Khim., 53 (1983) 901.
11 S. S. Iodko, O. L. Kaliya, O. L. Lebedev and E. A. Luk'yanets, Koord. Khim., 5 (1979) 611.
12 S. S. Iodko, O. L. Kaliya and O. L. Lebedev, Zh. Prik. Spektrosk., 26 (1977) 157.
13 T. I. Strelkova, G. P. Gurinovich and G. N. Sinyakov, Zh. Prik. Spektrosk., 4 (1966) 429.
14 D. Ledson and M. V. Twigg, Chem. Ind. (London), 3 (1975) 129; D. L. Ledson and M. V. Twigg, Inorg. Chim. Acta, 13 (1975) 43.
15 A. N. Sidorov and A. N. Terenin, Opt. Spektrosk., 11 (1961) 175 and 326.
16 A. G. Vinogradskii and A. N. Sidorov, Teor. Eksp. Khim., 18 (1982) 118.
17 A. G. Vinogradskii and A. N. Sidorov, Zh. Fiz. Khim., 55 (1981) 359.
18 J. F. Myers, G. W. Rayner-Canham and A. B. P. Lever, Inorg. Chem., 14 (1975) 461.
19 C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever and K. B. Tomer, Can. J. Chem., 63 (1985) 623.
20 W. A. Nevin, W. Liu, M. Melnik and A. B. P. Lever, J. Electroanal. Chem., 213 (1986) 217.
21 W. A. Nevin, M. R. Hempstead, W. Liu, C. C. Leznoff and A. B. P. Lever, Inorg. Chem., 26 (1987) 570.
22 G. P. Gurinovich, Spectroscopy of Chlorophyll and Related Compounds, US Joint Publications Research Service, Washington, DC, 1971.
23 B. D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanines, Wiley, New York, 1981.
24 K. N. Solovev, V. A. Mashenkov and T. F. Kachura, Opt. Spektrosk., 27 (1969) 24.
25 A. B. Anderson, T. L. Gordon and M. E. Kenney, J. Am. Chem. Soc., 107 (1985) 192.
26 P. D. Hale, W. J. Pietro, M. A. Ratner, D. E. Ellis and T. J. Marks, J. Am. Chem. Soc., 109 (1987) 5943.
27 T. Forster, Naturwissenschaften, 36 (1949) 36.
28 A. Weller, Prog. React. Kinet., 1 (1961) 189.
29 J. F. Ireland and P. A. H. Wyatt, Adv. Phys. Org. Chem., 12 (1976) 131.
30 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 2nd edn., 1984, p. 779.
31 M. J. Stillman and A. J. Thompson, J. Chem. Soc., Faraday Trans. 2, 70 (1974) 790.

32 A. B. P. Lever, *Phthalocyanines: Properties and Applications,* Vol. 2, VCH, New York, 1992.

33 D. W. Clack and J. R. Yandle, *Inorg. Chem., 11* (1972) 1738.

34 M. J. Stillman, *Phthalocyanines: Properties and Applications,* Vol. 2, VCH, New York, 1992.

35 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley, New York, 5th edn., 1988.

36 S. Zecevic, B. Simic-Glavaski, E. Yeager, A. B. P. Lever and P. C. Minor, *J. Electroanal. Chem., 196* (1985) 339.

37 P. A. Bernstein and A. B. P. Lever, *Inorg. Chem., 29* (1990) 608.

38 P. A. Bernstein, *Ph.D. Thesis,* York University, UK, 1991.

39 B. N. Achar, G. M. Fohlen, J. A. Parker and J. Keshavayya, *Polyhedron, 6* (1987) 1463.