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Photochemistry of Water-Soluble Porphyrins: Comparative Study of Isomeric Tetrapyridyl- and Tetrakis(*N*-Methylpyridiniumyl)porphyrins

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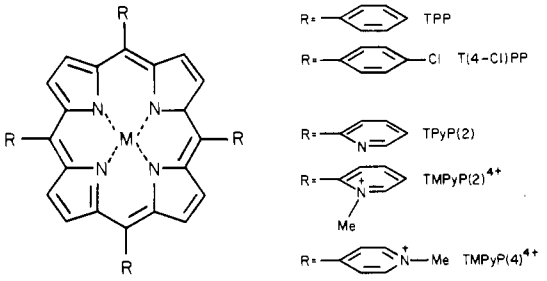
Photophysical properties (fluorescence spectra and lifetimes, quantum yields, triplet absorption, and phosphorescence spectra and lifetimes) have been studied for the three isomeric (ortho, meta, and para) free bases (H_2P), their diacid forms (H_4P^{2+}), and the zinc derivatives of tetrapyridyl- and tetrakis(*N*-methylpyridiniumyl)porphyrins (H_2TPyP, ZnTPyP, H_2TMPyP^{4+}, ZnTMPy^{4+}). While the excited-state properties are very similar for the three isomers of neutral TPyP with subtle differences, significant differences are shown to exist in the excited-state properties among the isomeric tetracationic porphyrins H_2TMPyP^{4+} and ZnTMPyP^{4+}.

Introduction

Tetrapyridylporphyrins (TPyP) along with tetraphenyl-



porphyrins (TPP) belong to a class of meso-substituted (substitution at the methine bridge of the porphine, see below) synthetic porphyrins that are readily synthesized and hence used widely as model compounds in various chemical and photochemical studies.[1-3] A series of water-soluble porphyrins are readily derived from these precursors by introduction of ionic groups such as $-COO^-$, $-SO_3^-$, $-N(CH_3)_3^+$, $-O^-$, etc. on the phenyl group of TPP and for TPyP by simple quaternization of the pyridyl N centers.[4-7] Toward development of a series of water-soluble porphyrin photosensitizers, we have been carrying out a systematic study of the photochemistry and redox chemistry of these porphyrin derivatives.[8-13] Most commonly studied porphyrins have been those that have the charged substituents at the para or 4-position.[14-21]

A major question in our studies has been the influence of these "peripheral charge groups" on the chemical, photochemical, and redox properties. Electron-withdrawing groups, while strongly raising the redox properties of the porphyrin macrocycle, also alter dramatically the kinetic reactivity as well. A correlation has also been shown to exist[22-25] between the basicity of the substituted porphyrin toward proton addition (as represented by the pK_a) and the kinetic and redox properties of the porphyrin. Earlier studies have shown that significant differences exist in the photophysical and redox properties of tetrapyridylporphyrins as compared to those of tetraphenylporphyrins, and at least part of these can be traced to the fact that, in general, TPyPs are considerably more acidic than the TPP-based systems. The electrochemical reduction behavior of para-substituted TPyPs also appears to be markedly different from that of the TPPs.[26-30] While the TMPyPs undergo two-electron reduction via stable phlorin intermediates, TPPs invariably yield chlorins.

Recently, Hambright and co-workers have shown[31-35] that large differences in the kinetic reactivity exist among the various isomeric forms (ortho or 2, meta or 3, and para or 4) of tetrakis(*N*-methylpyridiniumyl)porphyrins. The ortho isomer, H_2TMPyP(2)$^{4+}$, is unique in that it is the only porphyrin known to exist as a free base even in 1 N acid medium (a very acidic porphyrin with a pK_a of about −0.9). Herein we make a comparative study of the excited-state properties of the three isomeric forms of the free base and zinc derivatives of TPyP and TMPyP^{4+}. (Even though all the tetrakis(*N*-methylpyridiniumyl)porphyrins carry four positive charges on the peripheral substituents, for simplicity, hereafter we refer to the free bases, their diacid forms and zinc derivatives as H_2TMPyP, H_4TMPyP^{2+}, and ZnTMPyP, respectively.) It is shown that while the photophysical properties of the neutral isomeric porphyrins (H_2TPyP, ZnTPyP) are very similar,

(1) K. M. Smith, Ed., "Porphyrins and Metalloporphyrins", Elsevier, Amsterdam, 1975.
(2) D. Dolphin, Ed., "The Porphyrins", Vols. I–VII, Academic Press, New York, 1978.
(3) J. R. Darwent, P. Douglas, A. Harriman, G. Porter, and M.-C. Richoux, *Coord. Chem. Rev.*, **44**, 83 (1982).
(4) R. F. Pasternack, *Ann. N.Y. Acad. Sci.*, **206**, 614 (1973).
(5) P. Hambright in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 6, p 233.
(6) M. Krishnamurthy, *Indian J. Chem., Sect. B*, **15B**, 964 (1977).
(7) S. Sugata, S. Yamanouchi, and Y. Matsushima, *Chem. Pharm. Bull.*, **25**, 884 (1977).
(8) K. Kalyanasundaram and M. Grätzel, *Helv. Chim. Acta*, **63**, 478 (1980).
(9) M. Neumann-Spallart and K. Kalyanasundaram, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **36B**, 596 (1981).
(10) K. Kalyanasundaram and M. Neumann-Spallart, *J. Phys. Chem.*, **86**, 5163 (1982).
(11) K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2*, **79**, 1365 (1983).
(12) V. Houlding, K. Kalyanasundaram, M. Grätzel, and L. Migrom, *J. Phys. Chem.*, **87**, 3175 (1983).
(13) K. Kalyanasundaram, *Chem. Phys. Lett.*, **104**, 357 (1984).
(14) R. H. Schmehl and D. G. Whitten, *J. Phys. Chem.*, **85**, 3473 (1981).
(15) G. S. Nahor, J. Rabani, and F. Grieser, *J. Phys. Chem.*, **85**, 697 (1981).
(16) R. Bonnett, R. J. Ridge, E. J. Land, R. S. Sinclair, D. Tait, and D. G. Truscott, *J. Chem. Soc., Faraday Trans. 1*, **78**, 127 (1982).
(17) A. Harriman, G. Porter, and M.-C. Richoux, *J. Chem. Soc., Faraday Trans. 1*, **77**, 833 (1981).
(18) P. Neta, *J. Phys. Chem.*, **85**, 3678 (1981).
(19) N. Carnieri, A. Harriman, and G. Porter, *J. Chem. Soc., Dalton Trans.*, 931 (1982).
(20) K. Hatano and Y. Ischida, *Bull. Chem. Soc. Jpn.*, **55**, 3334 (1982).
(21) A. Harriman, G. Porter, and P. Walters, *J. Chem. Soc., Faraday Trans. 1*, **79**, 1335 (1983).
(22) P. Worthington, P. Hambright, R. F. X. Williams, M. R. Feldman, K. M. Smith, and K. C. Langry, *Inorg. Nucl. Chem. Lett.*, **16**, 441 (1980).
(23) A. N. Thompson and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **41**, 1251 (1980).
(24) A. Adeyemo, A. Shamin, P. Hambright, and R. F. X. Williams, *Indian J. Chem., Sect. A*, **21A**, 763 (1982).
(25) J. Turay and P. Hambright, *Inorg. Chem.*, **19**, 562 (1980).
(26) B. P. Neri and G. S. Wilson, *Anal. Chem.*, **44**, 1002 (1972).
(27) B. P. Neri and G. S. *Wilson*, *Anal. Chem.*, **45**, 442 (1973).
(28) D. L. Langhus and G. S. Wilson, *Anal. Chem.*, **51**, 1139 (1979).
(29) R. F. X. Williams and P. Hambright, *Bioinorg. Chem.*, **9**, 537 (1978).
(30) P. Hambright and R. F. X. Williams in "Porphyrin Chemistry Advances", F. R. Longo, Ed., Ann Arbor Science, Ann Arbor, MI, 1979, p 284.
(31) P. Hambright, T. Gore, and M. Burton, *Inorg. Chem.*, **15**, 2314 (1976).
(32) J. B. Reid and P. Hambright, *Inorg. Chem.*, **16**, 968 (1977).
(33) P. Hambright, *Inorg. Chem.*, **16**, 2987 (1977).
(34) A. Shamim and P. Hambright, *Inorg. Chem.*, **19**, 564 (1980).
(35) P. Hambright, *J. Inorg. Nucl. Chem.*, **39**, 1102 (1977).

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Table I. Absorption Spectral Features of Isomeric H_2TPyP and H_2TMPyP Tosylates and of $H_2T(Cl\text{-}P)P$

porphyrin	$pK_a(1)^c$	medium	abs peak ratios B(0,)	$Q_y(1,0)$	$Q_y(0,)$	$Q_x(1,0)$	$Q_x(0,0)$	$\epsilon[Q_y(1,0)]$, mM	$A[Q(0,0)]/A[Q(1,0)]$
$H_2TPyP(2)$	1.2	CH_2Cl_2	417 (19.5)	512 (1.0)	545 (0.35)	586 (0.35)	642 (0.14)	17.9	0.36
$H_2TPyP(3)$	2.1		418 (23.3)	512 (1.0)	547 (0.43)	588 (0.33)	646 (0.22)	24.0	0.49
$H_2TPyP(4)$	1.8		416 (25.1)	513 (1.0)	545 (0.29)	588 (0.31)	643 (0.13)	18.1	0.32
$H_2TMPyP(2)$	−0.9	H_2O	413 (14.6)	512 (1.0)	545 (0.20)	582 (0.33)	634 (0.09)	15.8	0.22
$H_2TMPyP(3)$	1.8		418 (17.0)	514 (1.0)	548 (0.20)	580 (0.38)	640 (0.08)	19.5	0.21
$H_2TMPyP(4)$	1.4		421 (15.6)	518 (1.0)	554 (0.37)	583 (0.41)	638 (0.09)	14.5	0.33
$H_2T(F)PP^a$		CH_2Cl_2	410 (14.2)	505 (1.0)	535 (0.12)	582 (0.32)	635 (0.05)	18.5	0.13
$H_2T(Cl\text{-}P)P(2)^b$		C_6H_6	418 (22.6)	513 (1.0)	543 (0.23)	589 (0.37)	645 (0.07)	16.4	0.22
$H_2T(Cl\text{-}P)P(3)^b$			420 (21.8)	513 (1.0)	547 (0.33)	589 (0.28)	645 (0.14)	20.7	0.37
$H_2T(Cl\text{-}P)P(4)^b$			419 (25.1)	514 (1.0)	550 (0.42)	590 (0.28)	646 (0.19)	20.4	0.48
H_2TPP^b	4.0		419 (25.1)	514 (1.0)	549 (0.41)	591 (0.29)	647 (0.18)	18.7	0.46

[a] Reference 11. [b] Reference 8. [c] $[H_2P]/[H_3P^+]$.

pronounced differences are observed among the three isomeric tetracationic porphyrins H_2TMPyP and ZnTMPyP. A comparison is also made with the "ortho effect" reported earlier[36-39] with the isomeric halogen-substituted tetraphenylporphyrins.

Experimental Section

Materials. Free-base porphyrins $H_2TPyP(2)$ and $H_2TPyP(3)$ were synthesized via Rothmund condensation with use of a modified Adler procedure.[40] Into a refluxing solution of propionic acid (100 mL) was slowly injected equimolar amounts of freshly distilled pyrrole and pyridine-2- or pyridine-3-carboxaldehyde, and the solution was allowed to reflux for about 45 min, after which the propionic acid was distilled off. The black residues were neutralized with NaOH, washed with methanol, dissolved in CH_2Cl_2, and chromatographed on a neutral Woelm alumina column prepared with acetone. After elution of a pale blue fraction, H_2TPyP is eluted with use of CH_2Cl_2 containing 5–10% pyridine. Shiny dark purple crystals are recovered from the dark red eluant after removal of solvents on a rotavaporator. Methylation of H_2TPyPs were carried out with use of methyl-*p*-toluenesulfonate in $CHCl_3$ as indicated by Hambright et al.[31] $H_2TPyP(4)$ and $H_2TMPyP(4)^{4+}$ were available from our earlier work.[10] Data on the molar absorption coefficients (H_2TPyPs in CH_2Cl_2 and $H_2TMPyPs$ in H_2O) are collected in Table I. These data are given for two reasons: they indicate the level of purity and also they have been used to calculate the excited-state absorption coefficients!) Incorporation of Zn^{2+} in the various isomeric porphyrins was carried out at room temperature with use of $ZnCl_2$. On the basis of an examination of the wealth of absorption spectral data for various porphyrins reported in the literature, we believe that, most often, for a given porphyrin, the relative peak ratios are very well reproduced in different laboratories, though not the absolute magnitude of the ϵ values. wherever comparison can be made, our data are in good agreement with the literature values.[4,7,27,31]

Photochemical Methods. Steady-state emission properties were recorded on a Perkin-Elmer MPF 4F spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 PM tube. Fluorescence spectra were recorded in the energy mode with subsequent manual correction for the PM-tube response. Fluorescence quantum yields were determined with use of H_2TPP in benzene ($\phi = 0.13$) and $ZnTMPy(4)^{4+}$ in water ($\phi = 0.025$) as standards. Fluorescence lifetimes were determined on a Applied Photophysics time-correlated single-photon counting unit. Laser photolysis studies were carried out on a fast kinetic spectroscopy unit employing the 15-ns, 530-nm light pulses from a Q-switched Nd laser as the excitation pulse. Triplet-state extinction coefficients were determined by saturation techniques and the quantum yields by comparison with known standards (ZnTPP, $\phi_T = 0.88$; $Ru(bpy)_3^{2+}$, $\phi = 1.0$). In the former, triplet absorbances are measured as a function of laser intensity up to complete conversion of the porphyrin to the $^3P^*$ state. In the latter the triplet quantum yield is determined by comparison of the concentration of the porphyrin transient with the concentration of triplets for a known standard, formed by the absorption of the same number of photons. Detail, as well as scope, limitations of both of these methods have been described earlier.[10,15,16,41,42] Estimated error limits on various measurements are as follows: τ_{trip}, ±10%; ϕ_{trip}, ±10%; ϵ_{T-T}, ±10%; τ_{fl}, ±20%; ϕ_{fl}, 10%.

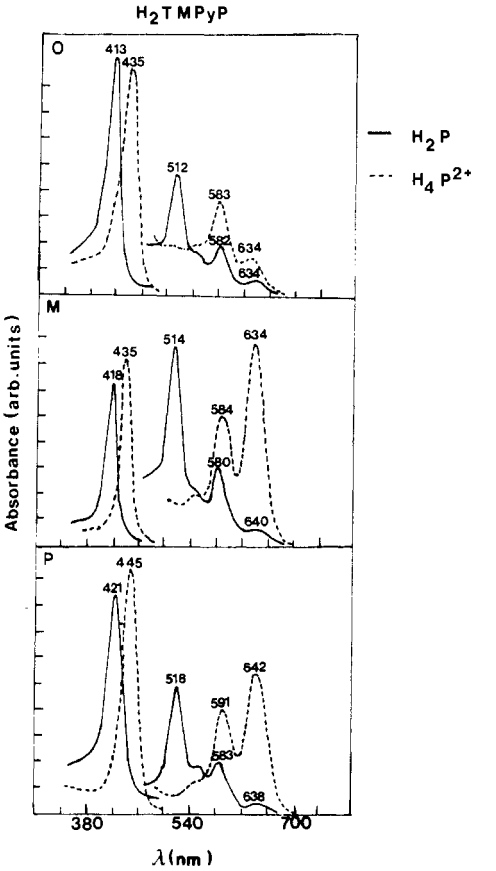

Figure 1. Absorption spectra of isomeric forms (ortho or 2, meta or 3, and para or 4) of tetrakis(*N*-methylpyridyl)porphyrins in aqueous solution at room temperature: (—) free-base forms (H_2P) at pH 6.0 and (---) diacid forms (H_4P^{2+}) in 1 N HCl (3, 4) and in 11 N HCl (2), respectively.

Results

Ground-State Absorption Spectra and Relative Basicity. Table I summarizes the absorption spectral features of the three isomers (ortho or 2, meta or 3, and para or 4) of H_2TPyP in CH_2Cl_2 and of the corresponding H_2TMPyP^{4+} in H_2O,

(36) J. B. Kim, J. J. Leonard, and F. R. Longo, *J. Am. Chem. Soc.*, **94**, 3986 (1972).
(37) D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.*, **97**, 5111 (1975).
(38) K. N. Solovev, M. P. Tsvirko, A. T. Gradyusho, and D. T. Kozlich, *Opt. Spectrosc. (Engl. Transl.)*, **33**, 871 (1972).
(39) G. D. Egorova, V. N. Knyukshto, K. N. Solovev, and M. P. Tsvirko, *Opt. Spectrosc. (Engl. Transl.)*, **48**, 1101 (1980).
(40) M. A. Torrens, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4160 (1972).
(41) J. T. Richards and J. K. Thomas, *Trans. Faraday Soc.*, **66**, 621 (1970).
(42) B. Amand and R. Bensasson, *Chem. Phys. Lett.*, **34**, 44 (1975).

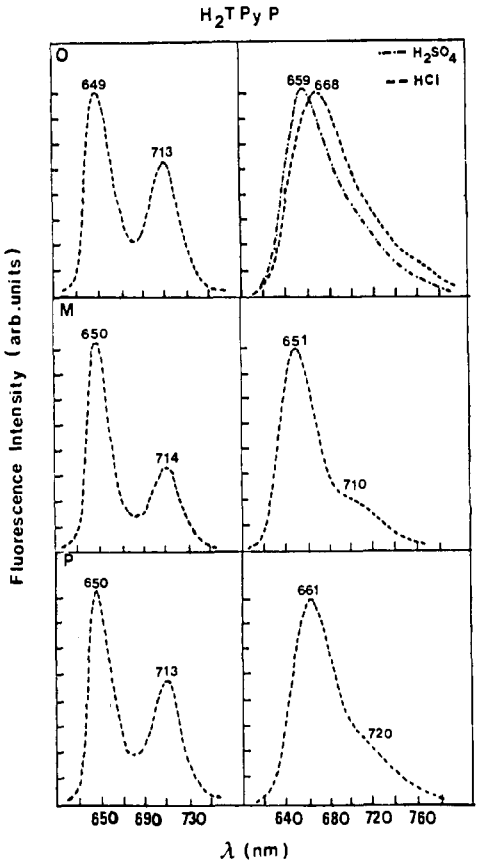

Figure 2. Fluorescence spectra of the three isomers (ortho or 2, meta or 3, and para or 4) of H_2TPyP. Spectra on the left are emissions from the free bases in CH_2Cl_2 and on the right emissions from the diacid forms in 1 N HCl.

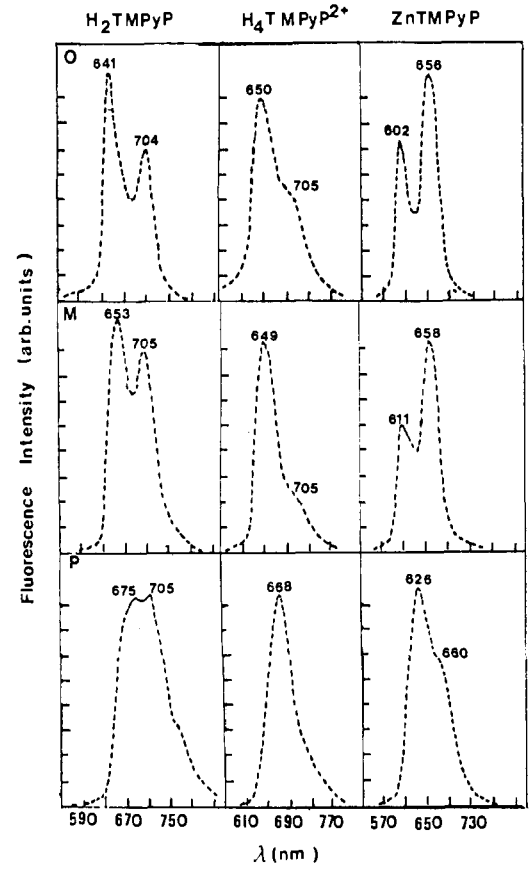

Figure 3. Fluorescence spectra of the three isomers (ortho or 2, meta or 3, and para or 4) of H_2TMPyP (free-base forms in aqueous solution, pH 6.0), H_4TMPyP^{2+} (diacid forms in 11 N HCl), and $ZnTMPyP^{4+}$ (aqueous solution, pH 6.0).

along with the pK_a values for the formation of monoacid cations of these from their free bases (eq 1). Absorption

$$H_2P + H^+ \rightleftharpoons H_3P^+ \quad pK_a(1) \qquad (1)$$

intensities are correlated in terms of the relative peak ratios normalized with respect to the Q(1,0) band, for it is known[43-46] that this Q(1,0) band is rather insensitive to the nature of the substituents. Following Gouterman et al.,[44] we have given in the last column of Table I the absorbance ratio Q(0,0)/Q(1,0) (eq 2) as a measure of the substituent effect on the absorption

$$Q(0,0)/Q(1,0) = [Q_x(0,0) + Q_y(0,0)]/[Q_x(1,0) + Q_y(1,0)] \qquad (2)$$

properties. For comparison we have included similar data from the literature on the isomeric chloro-substituted H_2TPPs[36,37] and on the perfluorosubstituted H_2TPPs.[44] Figure 1 presents a comparison of the absorption spectra of isomeric $H_2TMPyPs$ both as free bases and as diacids.

Examination of the data presented shows several features of the isomeric tetrapyridylporphyrins: (i) As with the isomeric $H_2T(x\text{-Cl})PPs$, the absorption maxima are strikingly similar both in H_2TPyPs and in $H_2TMPyPs$. Along the series *p*-, *m*-, and *o*-$H_2TMPyPs$, there is a small but persistant blue shift in the absorption maxima of the Soret and $Q_y(1,0)$ bands. (ii) As with H_2TPPs, the splitting of the Q(1,0) band into $Q_y(1,0)$ and $Q_x(1,0)$ in H_2TPyPs has a separation of 2500 cm^{-1}. (iii) The intensities of Q(0,0) bands are distinctly weaker in the ortho and para isomers as compared to meta. (iv) Absorption of Soret and Q bands are significantly lower in all of the isomeric $H_2TMPyPs$.[47]

Table II. Fluorescence Properties of Isomeric H_2TPyP and H_2TMPyP Tosylates along with Those of $H_2T(Cl\text{-}P)P$

porphyrin	medium	fluor max, nm (rel intens) Q(0,0)	Q(0,1)	τ_{fl}, ns	ϕ_{fl}
$H_2TPyP(2)$	CH_2Cl_2	639 (1.55)	712 (1.0)	9.0	0.060
$H_2TPyP(3)$		650 (2.53)	714 (1.0)	7.8	0.066
$H_2TPyP(4)$		649 (1.73)	713 (1.0)	8.5	0.072
$H_2TMPyP(2)$	H_2O	641 (1.28)	704 (1.0)	13.8	0.086
$H_2TMPyP(3)$		653 (1.53)	705 (1.0)	7.9	0.049
$H_2TMPyP(4)$		675 (0.98)	705 (1.0)	6.0	0.047
$H_2T(F)PP^a$	CH_2Cl_2	631 (0.20)	698 (1.0)		0.07
$H_2T(Cl\text{-}P)P(2)^b$	C_6H_6	652 (0.30)	717 (1.0)		0.02
$H_2T(Cl\text{-}P)P(3)^b$		652 (0.85)	718 (1.0)		0.08
$H_2T(Cl\text{-}P)P(4)^b$		653 (1.10)	720 (1.0)		0.09
H_2TPP^b		652 (1.11)	718 (1.0)	13.6	0.11

[a] Reference 11. [b] Reference 8.

(43) M. Gouterman in "The Porphyrins", D. Dolphin, Ed., Vol. III, Academic Press, New York, 1978, Chapter 1.
(44) P. J. Spellane, M. Gouterman, A. Antipas, S. Kim, and Y. C. Lin, *Inorg. Chem.*, **19**, 386 (1980).
(45) M. H. Perrin, M. Gouterman, and C. L. Perrin, *J. Chem. Phys.*, **50**, 4137 (1969).
(46) The Q(1,0) absorption and the corresponding Q(0,1) emission band of the isomeric TPyPs and TMPyPs do show some variation in the position as well in intensity. But these variations are much smaller (position ±2 nm, intensity ±30%) as compared to that observed in the Q(0,0) band (position >6–8 nm and intensity variations up to 300%).
(47) Earlier studies with isomeric substituted tetraphenylporphyrins[7,36,48] have shown that "electron-withdrawing character of the substituent in *meso*-tetraphenylporphyrins reduces the absorption intensities due to the (0,0) transition whereas electron-donating character increases them". Most often, this is also reflected in their emission spectra as well.[37,39]
(48) M. Meot-Ner and A. D. Alder, *J. Am. Chem. Soc.*, **97**, 5107 (1975).

Table III. Absorption and Fluorescence Properties of Isomeric Zinc Porphyrin Derivatives: ZnTPyP, ZnTMPyP, and ZnT(Cl-P)P

porphyrin	medium	abs peak ratios B(0,0)	abs peak ratios Q(1,0)	abs peak ratios Q(0,0)	ϵ[Q(1,0)], mM	fluor max, nm (rel intens) Q(0,0)	fluor max, nm (rel intens) Q(0,1)	ϕ_{fl}
ZnTMPyP(2)	H_2O	426 (14.7)	556 (1.0)	590 (0.28)		602 (0.71)	656 (1.0)	0.028
ZnTMPyP(3)		428 (16.8)	558 (1.0)	594 (0.20)		611 (0.60)	658 (1.0)	0.017
ZnTMPyP(4)		436 (11.3)	560 (1.0)	602 (0.33)	16.0	626 (1.53)	~660 (1.0)	0.025
ZnTPyP(2)	DMF	426 (23.9)	554 (1.0)	593 (0.26)		610 (0.71)	654 (1.0)	
ZnTPyP(3)		428 (25.1)	555 (1.0)	596 (0.21)		605 (1.10)	655 (1.0)	
ZnTPyP(4)		426 (20.9)	556 (1.0)	592 (0.30)		610 (0.80)	654 (1.0)	
ZnT(Cl-P)P(2)[a]	C_6H_6	422 (22.3)	550 (1.0)	588 (0.07)	23.7	594 (0.18)	646 (1.0)	0.038
ZnT(Cl-P)P(3)[a]		423 (22.6)	549 (1.0)	588 (0.12)	23.8	600 (0.43)	648 (1.0)	0.017
ZnT(Cl-P)P(4)[a]		424 (23.0)	550 (1.0)	589 (0.16)	24.1	600 (0.58)	648 (1.0)	0.02
ZnTPP[a]		423 (23.8)	548 (1.0)	586 (0.16)	22.8	598 (0.54)	647 (1.0)	0.033
ZnT(F)PP[b]	CH_2Cl_2	412	543 (1.0)	578 (0.26)	20.9	585 (0.21)	641 (1.0)	

[a] Reference 8. [b] Reference 11.

pK_a values of free bases are a very sensitive measure of the degree of interaction of the peripheral substituents with the porphine macrocycle. The isomeric H_2TPyPs and H_2TMPyPs are considerably more acidic than the H_2TPPs because of the better electron-withdrawing character of the pyridyl groups. The pK_a values of the isomeric H_2TPyPs are in the range of 1.2–2.1, and these decrease further upon methylation of the pyridyl N centers.[31-35] The relative shift in pK_a(1) upon methylation is about 0.3–0.4 unit for the meta and para isomers while it is nearly 2 pH units for the ortho isomer. Also, among the three isomers, the relative order of pK_a is meta > para > ortho.

Fluorescence in Solution. The emission behavior of the three isomeric porphyrin derivatives has been examined in solution at room temperature (H_2TPyPs in CH_2Cl_2 and H_2TMPyPs in H_2O), and Figures 2 and 3 present a collection of such spectra. Quantitative data on the emission maxima, relative intensities, quantum yields, and lifetimes of emission are collected in Tables II and III. As with the absorption data, for comparison, we have included in these tables emission data on the isomeric H_2T(x-Cl)PPs and on H_2TFPP. Tetrakis(perfluorophenyl)porphyrin is also unique in showing large differences in the absorption and emission behavior as compared to simple H_2TPP.

The fluorescence spectra of the three isomeric neutral H_2TPyPs are strikingly similar among themselves as well as with H_2TPP. The relative intensity of the Q(0,0) band in emission follows the same order meta > para > ortho, as observed in the absorption spectra and in the pK_a values. The fluorescences of the H_2TMPyP^{4+} isomers (all tetracationic!) show a marked difference from each other. While the position of the Q(0,1) band remains unaltered, the Q(0,0) band shifts significantly. Along the series ortho, meta, and para, there is a gradual red shift in the position of the Q(0,0) band. Thus, while the Q(0,0) and Q(0,1) bands are well resolved in the ortho isomer, they merge into a broad band with a shoulder in H_2TMPyP(4). The relative intensity of the Q(0,0) band with respect to the Q(0,1) band, however, retains the same order as in the neutral H_2TPyPs. Since the positions of the Q(0,0) band in the absorption of H_2TMPyPs are rather similar, the large red shifts in the Q(0,0) band of fluorescence implies a large Stokes shift in the meta and para isomers (759 and 311 cm^{-1}, respectively) as compared to that in the ortho isomer (172 cm^{-1}).

All the free-base porphyrins under study are moderately fluorescent with quantum yields in the range of 5–10%. As in the absorption and emission spectra, the quantum yields and lifetimes of isomeric H_2TPyPs are very similar (ϕ = 6–7% and τ = 8–9 ns). As regards the tetracationic H_2TMPyPs, the ortho isomer is remarkable in having fluorescence quantum yield and lifetime almost twice that of the meta and para isomers. For all the free-base porphyrins, the natural radiative lifetimes $\tau_{nat} = \tau_{fl}/\phi_{fl}$ are within 115–150 ns, the range observed with a variety of free-base porphyrins. The peculiar "ortho effect" observed with H_2TMPyP(2)$^{4+}$ is reminiscent of the "ortho effect" observed earlier with H_2T(2-Cl)PP. It has been reported that the quantum yield of fluorescence of *o*-chloro-substituted TPP is distinctly lower (by a factor of 2) as compared to meta- and para-substituted free bases, but an inverse trend was observed with their respective Zn porphyrin systems.[37,39]

Table IV. Triplet Excited-State Properties of Isomeric H_2TPyP (Free Base and Diacid Forms), H_2TMPyP, and ZnTMPyP Tosylates at Room Temperature

porphyrin	medium	T-T abs max, nm (ϵ, mM)	τ_{trip}, ms	ϕ_{trip}	phos max (77 K), nm
H_2TPyP(2)	CH_2Cl_2	790 (2.6), 695	0.15		860
H_2TPyP(3)		790 (3.6), 700	0.17		860
H_2TPyP(4)		790 (3.8), 695	0.17	0.90	860
H_2TMPyP(2)	H_2O	790 (2.6)	1.16		860
H_2TMPyP(3)		840 (3.2), 710	0.39		860
H_2TMPyP(4)		920 (7.6), 820	0.17	0.92	860
ZnTMPyP(2)		850, 750	1.4		768
ZnTMPyP(3)		830, 750	2.0		760
ZnTMPyP(4)		1020 (7.2), 950	2.0	0.90	770
H_2TPyP(2)	1 N HCl	930, 720			
H_2TPyP(3)		890, 720			
H_2TPyP(4)		950, 720			

Absorption and Fluorescence of Zinc Porphyrins. The pronounced differences observed in the absorption and emission properties of the isomeric H_2TPyP and H_2TMPyP^{4+} compounds are reflected in their zinc derivatives as well, and data on these are summarized in Table III. The fluorescence maxima of the ZnTPyPs are very similar and are red shifted by about 6–8 nm with respect to that of ZnTPP. The Stokes shift is about 250–310 cm^{-1} in the isomeric ZnTPyPs and is increased twice as much in ZnTMPyP(4)$^{4+}$. (The values are 338, 468, and 637 cm^{-1} for the ortho, meta, and para isomers, respectively). There is also the inversion in the relative peak intensities of the Q(0,0) band, meta > para > ortho. The quantum yields of fluorescence show only a small variation among the isomeric ZnTMPyPs, with the relative order ortho > para > meta. The natural radiative lifetimes are in the range of 40–50 ns for all the isomeric TPyPs and TMPyPs, values somewhat lower than that of tetraphenylporphyrins.

Triplet Excited States. Like the tetraphenylporphyrins, the tetrapyridylporphyrins have triplet-state production with a high quantum yield and the triplets are readily monitored via their $T_0 - T_n$ absorption with use of a flash photolysis setup. Figure 4 presents a series of such $T_0 - T_n$ absorption spectra for the three isomeric forms of H_2TPyP, H_2TMPyP^{4+}, and ZnTMPyP^{4+}. Data on the triplet excited state lifetimes and quantum yields for intersystem crossing as well as extinction

Table V. Absorption and Fluorescence Properties of Diacid Forms of Isomeric H_2TPyP and of H_2TMPyP Tosylates

porphyrin	medium	abs peak ratios			ϵ[Q(1,0)], mM	fluor max, nm (rel intens)	
		B(0,0)	Q(1,0)	Q(0,0)		Q(0,0)	Q(0,1)
$H_2TPyP(2)$	1 N HCl	438 (18.3)	585 (1.0)	633 (0.70)	10.8	668 (3.66)	~720 (1.0) (?)
	1 N H_2SO_4					659 (4.20)	~720 (1.0)
$H_2TPyP(3)$	1 N HCl	434 (27.8)	585 (1.0)	633 (1.55)	11.0	651 (4.47)	~710 (1.0)
$H_2TPyP(4)$		442 (24.1)	588 (1.0)	639 (1.31)	11.2	661 (4.10)	~720 (1.0)
$H_2TMPyP(2)$	11 N HCl	435 (19.3)	582 (1.0)	634 (0.55)	12.0	650 (1.90)	705 (1.0)
$H_2TMPyP(3)$	1 N HCl	435 (28.4)	584 (1.0)	634 (1.54)	12.5	649 (3.80)	705 (1.0)
$H_2TMPyP(4)$		445 (21.0)	591 (1.0)	642 (1.30)	12.0	668 (4.00)	715 (1.0)
H_2TPP	acetone/HCl	445 (41.3)	608 (1.0)	662 (5.0)	9.0	689 (6.37)	760 (1.0)

coefficients are collected in Table IV. As in our earlier studies, for the reason of extensive photolysis of the porphyrins by the analyzing light, we have monitored the $T_0 - T_n$ absorption in the red to near-IR region using an ITT photodiode, which has a good response up to 1200 nm.

The $T_0 - T_n$ absorption spectra are distinctly different for the various isomeric porphyrin derivatives. As in the absorption and fluorescence spectra, the $T_0 - T_n$ spectra and triplet lifetimes of the neutral isomeric H_2TPyPs are very similar with the farthest absorption band located at ca. 790 nm. In the free-base porphyrins, while the methylation hardly produces any shift in the ortho isomer, there are about 50- and 130-nm red shifts of the longest wavelength absorption in the meta and para isomers, respectively. Incorporation of Zn^{2+} causes significant shifts in the ortho and para isomers, but for the meta isomer there is hardly any shift.

The triplet lifetimes also undergo drastic changes upon methylation of H_2TPyP as well as metalation with Zn^{2+}. The triplet lifetimes of isomeric H_2TPyPs are very similar (ca. 170 μs) but are significantly lower as compared to H_2TPP. There is a decrease in the lifetime along the series ortho > meta > para in the $H_2TMPyPs$. As is observed with other Zn porphyrin systems, the lifetimes of triplets of the three isomeric ZnTMPyPs are in the range of 1.4–2.0 ms. The quantum yields for intersystem crossing are rather high (>0.85) for all the free-bases and zinc porphyrins under study.

As in the past,[49] attempts to monitor the phosphorescence emission of the free-base porphyrins at low temperature (77 K) had only limited success. For both the H_2TPyPs and $H_2TMPyPs$, we could roughly locate very weak emission around 860 nm ($\phi \leq 10^{-5}$) and it is not influenced in any way by the use of heavy-atom solvents such as ethyl iodide. Phosphorescence of zinc porphyrins, however, is readily observed at 77 K, and within ± 4 nm, the phosphorescence maxima are similar for all of the isomeric ZnTPyPs (in ethyl ether/isopropyl alcohol 1:1 glass) and ZnTMPyPs (water/glycerol 1:1 glass). Thus the phosphorescence maxima of ZnTPyPs are blue shifted by about 20 nm with respect to that of ZnTPP. The estimated triplet excited state energies for the free bases and zinc derivatives are 1.44 and 1.63 eV, respectively (for both TPyPs and TMPyPs). (Excited-States energies based on the emission maxima are lower limits, for they include a contribution from vibrational distortions between the ground and excited states and not true energy differences between the two thermally equilibrated states!) The above estimates for the triplet excited-state energy give, in turn, the singlet-triplet separation of about 0.47 and 0.40 eV for the isomeric free bases and ZnTPyPs, respectively. Because of the gradual red shift of the Q(0,0) fluorescence band, the S–T separation of $H_2TMP(2)^{4+}$ is larger by about 0.10 eV as compared to that of the corresponding para isomer.

Photochemistry of Diacid Forms of the Free Base Porphyrins. The chemistry of the diacid forms of the free-base porphyrins have not been well studied, especially in the excited state.[50-52] Pronounced differences have been observed if one examines the absorption spectral features of the diacid forms of the isomeric H_2TPyPs and H_2TMPyP tosylates, and Table V presents a collection of such data (for absorption spectra, see Figure 1). In diacid forms, the porphyrin skeleton recovers its D_{4h} symmetry as in metalloporphyrins with closed-shell metal ions and there are only two visible bands, Q(0,0) and Q(1,0), in addition to the Soret or B(0,0) band. For both H_4TPyP^{2+} and H_4TMPyP^{2+}, the Q(0,0) band has maximum intensity in the meta isomer and decreases as one goes through the series meta > para > ortho. The absorption intensity of

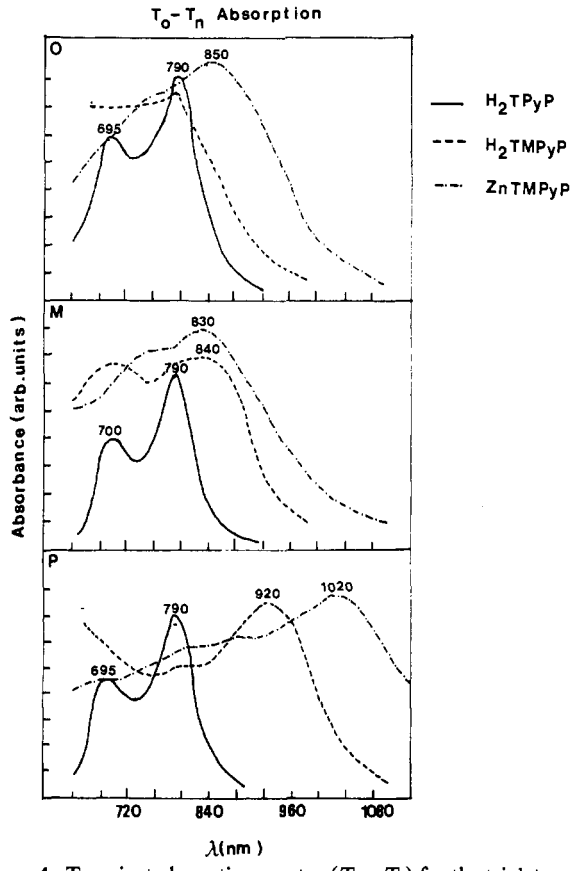

Figure 4. Transient absorption spectra ($T_0 - T_n$) for the triplet excited state of the three isomers (ortho or 2, meta or 3, and para or 4) of H_2TPyP (in CH_2Cl_2), H_2TMPyP (in aqueous solution, pH 6.0), and $ZnTMPyP^{4+}$ (in aqueous solution, pH 6.0) recorded at the end of the laser pulse.

(49) M. Gouterman and G. E. Khalil, *J. Mol. Spectrosc.* **53**, 88 (1974).

(50) Absorption and emission spectra of the dication and dianion of H_2EtioP and H_2TPP: E. Austin and M. Gouterman, *Bioinorg. Chem.*, **9**, 281 (1978).

(51) Crystal structure study of H_4TPP^{2+} and of H_4TPyP^{2+}: A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, **90**, 2735 (1968).

(52) Triplet spectra of free base and mono- and dications of protoporphyrin IX: R. S. Sinclair, D. Tait, and T. G. Truscott, *J. Chem. Soc., Faraday Trans. 1*, **768**, 417 (1980).

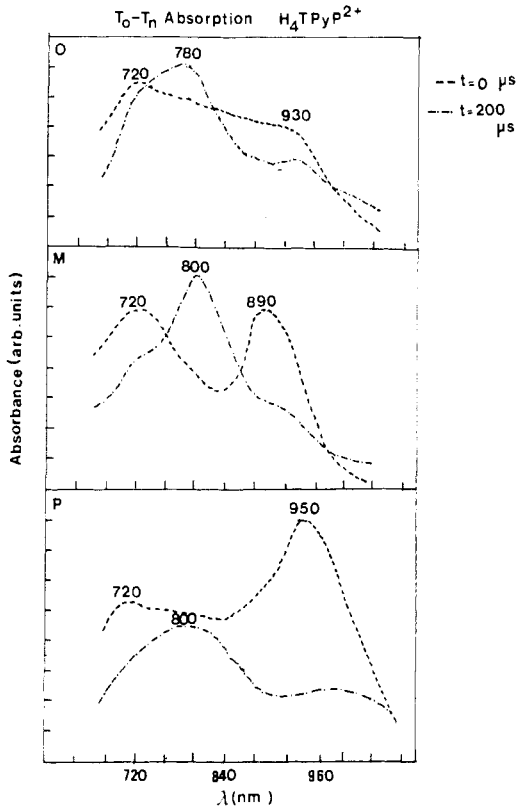

Figure 5. Transient absorption spectra ($T_0 - T_n$) for the triplet excited state of the three isomers (ortho, meta, and para) of H_2TPyP in the diacid form in 1 N HCl: (---) spectra recorded at the end of the laser pulse; (—·—) spectra recorded at 200 μs after the excitation pulse.

the Soret Band (ϵ) also follows the same order. The relative order as well as absolute intensities of absorption reflect the same trend observed in the pK_a values of these free-base porphyrins to form the mono- and diacid forms. There is a considerable weakening of the absorption in the Soret and Q bands as one increases the electron-withdrawing character of the methine bridge substituent. As in the free-base forms, the para isomers of H_2TPyP and H_2TMPyP in the diacid form show the maximum red shift of the absorption maxima. Due to the rather low value of pK_a(1) of −0.9, the diacid form of $H_2TMPyP(2)^{4+}$ is observed only in pure/concentrated acid media (>10 N).

The fluorescence spectra of the diacid forms of meta and ortho isomers of free-base TPyP and TMPyP are very similar. In all cases, the fluorescence spectra are poorly resolved as compared to those of the neutral free-base forms. While the absorbance and fluorescence of free-base forms of H_2TPyP and H_2TPP are very similar, in the diacid forms, the fluorescence of H_4TPyP^{2+} compounds is blue shifted by about 20 nm relative to that of H_4TPP^{2+}. The shift in the absorption maxima has been attributed earlier by Stone and Fleischer[51] to differences in the crystal structures of the diacid forms. The fluorescence spectra of the ortho and meta isomers are indepedent of the nature of the acid medium (HCl, HNO_3, H_2SO_4) while the para isomer $H_4TMPyP(4)^{2+}$ is very sensitive to the nature of the anion. (In HCl, the maximum is at 668 nm and is blue shifted to 659 nm in H_2SO_4). Similar anion dependence of fluorescence of H_4TPP^{2+} has been reported earlier by Gouterman et al.[50] In all cases, the fluorescence lifetimes for the diacid emission are considerably shorter (< ns).

The possibility of monitoring the triplet of the diacid forms of the TPyPs via their $T_0 - T_n$ has also been explored by nanosecond laser photolysis. Figure 5 presents the transient absorption spectra (recorded at the end of the laser pulse) upon excitation with 15-ns, 530-nm, light pulses of the isomeric H_4TPyP^{2+} compounds in 1 N HCl. For the three isomers, one can locate two broad maxima, one at ca. 720 nm and another between 890 and 950 nm. The relative intensities of the two peaks vary considerably as one goes through the series ortho, meta, and para. The end of the laser pulse transient decays over 200 μs to yield a second transient, whose spectrum is also plotted in Figure 5. The second transient slowly decays over a few milliseconds. On the basis of the similarity of these second transients to that of phlorin monoanions reported earlier,[27] we tentatively assign this to the monoanions generated via in situ reduction of the triplet with the solvent acid/anion (eq 3). We are in the process of a more elaborate study aimed toward elucidation of the reduction products' formation and their mode of decay.

$$H_4TPyP^{2+*} + H^+ + e^-(S) \rightarrow H_5TPyP^{2+} \qquad (3)$$

Discussion

The relative differences among the isomeric TPyPs in the ground and excited states are rather subtle, for they reflect the small differences in the influence of the electron-withdrawing character of the pyridyl group. The differences among the isomeric tetrakis(*N*-methylpyridiniumyl)porphyrins in the photophysical properties are more pronounced than in the TPyPs. Since the latter are electrically neutral and TMPyPs carry 4+ charges on the peripheral substituents, it is tempting to attribute the differences as due to the presence of high peripheral charges. However, such interpretations of effects as solely due to the presence of positive or negative charges on the periphery without regard to the extent of interaction of the substituent groups with the porphine ring are rather crude. We have shown earlier[11] that, due to the inefficient interaction of the phenyl groups with the porphine ring, the photophysical and redox properties of neutral TPP (tetraphenylporphin), tetracationic $TAPP^{4+}$ (tetrakis((trimethylamino)phenyl)porphyrin), and tetraanionic $TPPS^{4-}$ (tetrakis(4-sulfonatophenyl)porphyrin) are all very similar. A better guide to measure the extent of charge (resonance and inductive) effects of peripheral substituents is given by the pK_a of the free bases for proton uptake. As we pointed out in the Introduction, a correlation exists between the basicity of a substituted porphyrin toward proton uptake (as represented by the pK_a) and the kinetic and redox properties of the porphyrin. (The pK_a is a measure mainly of σ charge density in the porphyrin ring, yet the spectral and electrochemical redox changes being interpreted are in the π-electron system. The σ charge does indirectly influence the π orbitals by affecting the Coulomb integrals of the meso carbons).

Methylation of the pyridyl N centers in addition to attribution of positive charges to the substituent group can introduce significant steric effects to prevent/enhance the effective delocalization of the charge density on the porphyrin. It has been suggested that the inefficient influence of the phenyl groups of TPP is due to the nonplanarity of the phenyl groups with the porphyrin π system. If so, then, the steric effects of the *N*-Me groups in TMPyPs would seem to play a negative role in bringing the pyridyl/phenyl groups more in plane with the porphyrin ring, especially for the ortho isomer. The ortho methyl group prevents rotation into the plane. The nearly 2 pH unit shift in the pK_a of *o*-H_2TPyP upon methylation toward more acidity presumably reflects the occurrence of such a process. Thus, the differences in the behavior of isomeric TMPyPs are due to the combined effects of steric, resonance, and inductive effects. If steric effects do play a dominant role, then, one could anticipate a similar spread in pK_a of about 3 pH units among the isomeric (ortho, meta, and para) $TAPP^{4+}$ tetrakis((trimethylamino)phenyl)porphyrin) compounds as well. Photochemically, isomeric tetrakis(halogenophenyl)-porphyrins have been the only porphyrin system that has been

explored to date to study this "ortho effect".

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Note Added in Proof. Recently, ortho effects arising from steric factors have been shown to cause large differences in the ground- and excited-state properties of tetrakis(2,6-dimethylphenyl)porphyrin and its sulfonato derivative.[53]

Registry No. ZnTMPyP(2), 59729-18-9; ZnTMPyP(3), 59729-16-7; ZnTMPyP(4), 40603-58-5; ZnTPyP(2), 59729-19-0; ZnTPyP(3), 59729-17-8; ZnTPyP(4), 31183-11-6; ZnT(Cl-P)P(2), 56811-36-0; ZnT(Cl-P)P(3), 56811-38-2; ZnT(Cl-P)P(4), 29116-33-4; ZnTPP, 14074-80-7; ZnT(F)PP, 72076-08-5; H_2TPyP(2), 40904-90-3; H_2TPyP(3), 40882-83-5; H_2TPy(4), 16834-13-2; H_2TMPyP(2), 59728-89-1; H_2TMPyP(3), 59728-91-5; H_2TMPyP(4), 38673-65-3; H_2T(F)PP, 25440-14-6; H_2T(Cl-P)P(2), 22112-77-2; H_2T(Cl-P)P(3), 37083-39-9; H_2T(Cl-P)P(4), 37083-35-5; H_2TPP, 917-23-7.

(53) W. A. Lee, M. Grätzel, and K. Kalyanasundaram, *Chem. Phys. Lett.*, **107**, 308 (1984).

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Magnetic Interactions in Copper Complexes of Tetradentate Binucleating Phthalazine Ligands. Crystal and Molecular Structure of Binuclear μ-Hydroxo-Bridged Copper(II) Complexes of 1,4-Bis(2-pyridylamino)phthalazine and 1,4-Bis((4-methyl-2-pyridyl)amino)phthalazine

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The dimensions of the binuclear centers in a series of triply bridged binuclear copper(II) complexes involving both a diazine (N–N) and a μ-hydroxo bridge can be varied (tuned) as a result of changing the third anionic bridge group. Cu–O–Cu bridge angles in the range 100–116° are found by varying the anionic bridge from Cl^- to SO_4^{2-}. The crystal and molecular structure of $[Cu_2(PAP4Me)(OH)(H_2O)_2(NO_3)_2]NO_3$ (I) (PAP4Me = 1,4-bis((4-methyl-2-pyridyl)amino)phthalazine) and $[Cu_2(PAP)(OH)Cl(SO_4)]\cdot 2H_2O$ (II) (PAP = 1,4-bis(2-pyridylamino)phthalazine) are reported and the dimensions of the binuclear centers (e.g. Cu–O–Cu angles and Cu–Cu separation) compared with those of other related complexes in the light of antiferromagnetic exchange between the copper(II) centers. I crystallizes in the monoclinic system, space group $P2_1/a$, with a = 27.078 (1) Å, b = 13.4451 (4) Å, c = 7.3744 (6) Å, β = 105.575 (4)°, and four formula units per unit cell. II crystallizes in the monoclinic system, space group $P2_1/a$, with a = 17.2850 (7) Å, b = 9.5248 (6) Å, c = 14.5520 (7) Å, β = 117.198 (3)°, and four formula units per unit cell. Refinement by "block-diagonal least squares" gave final R factors of 0.039 (I) and 0.030 (II). Both copper atoms in I are distorted six-coordinate, with bridging nitrate and hydroxide groups, a Cu···Cu separation of 3.138 Å, and a Cu–O–Cu bridge angle of 115.3°. In II distorted-square-pyramidal copper centers are found, with bridging sulfate and hydroxide groups, a Cu···Cu separation of 3.211 Å, and a Cu–O–Cu bridge angle of 115.5°. The sulfate acts both as a bidentate intramolecular bridge and also as a tridentate intermolecular bridge. Magnetic susceptibilities of solid samples were determined in the range 77–300 K, and in both cases the systems conform to the Van Vleck equation for exchange-coupled pairs of copper(II) ions with $-2J$ = 497 cm^{-1} (I) and $-2J$ = 532 cm^{-1} (II).

Introduction

Binuclear copper(II) complexes with nitrogen donor ligands and hydroxide or oxygen-containing bridges between the metal centers usually exhibit antiferromagnetic coupling and are potential models for binuclear copper protein centers which take part in biological reactions involving molecular oxygen, such as oxygen transport[2] and oxygen activation.[3,4] Such binuclear copper centers are found in, e.g., the oxygen carrier hemocyanin[5] and the monooxygenase tyrosinase.[6] Magnetic measurements on protein extracts indicate strong antiferromagnetic exchange between the copper(II) centers in *Rhus vernicifera* laccase[7] ($-2J \geq 1000$ cm^{-1}) and in oxyhemocyanin (*Megathura crenulata*; $-2J \geq 1250$ cm^{-1}).[7,8] An oxygen-containing group has been suggested as the bridging entity between the copper(II) centers in these proteins and is thought to be primarily responsible for the exchange.[9,10] Strong antiferromagnetic exchange is observed in binuclear copper(II) systems involving single hydroxide bridges. For the complexes $[Cu_2(tren)_2(OH)](PF_6)_3$ and $[Cu_2(tren)_2(OH)](ClO_4)_3\cdot H_2O$, in which the hydroxide group appears to act as the only bridge between the metal centers, exchange integrals of $-2J$ = 700 and 760 cm^{-1} are respectively observed.[11] In the complex $[Cu_2(L)(OH)](BF_4)_3$ (L = 1,4-bis((1-oxa-4,10-dithia-7-aza-cyclododecan-7-yl)methyl)benzene) in which, in addition to

(1) (a) Memorial University of Newfoundland. (b) National Research Council.
(2) Lontie, R.; Vanquickenborne, L. *Met. Ions Biol. Syst.* **1974**, *3*, 183.
(3) Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1.
(4) (a) Vanneste, W. H.; Zuberbühler, A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974, and references therein. (b) Ochiai, E. "Bioinorganic Chemistry, An Introduction"; Allyn and Bacon: Boston, 1977, and references therein.
(5) (a) Bannister, J. V., Ed. "Structure and Function of Hemocyanin"; Springer-Verlag: Berlin, 1977. (b) Lontie, R.; Witters, R. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; p 229.
(6) (a) Urbach, F. L. *Met. Ions Biol. Syst.* **1981**, *13*, 73 and references therein. (b) Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; p 41. (c) Lerch, K. *Met. Ions. Biol. Syst.* **1981**, 13, 143.
(7) Dooley, D. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3019.
(8) Solomon, E. I.; Dooley, D. M.; Wang, R. H.; Gray, H. B.; Cerdonio, M.; Mogno, F.; Romani, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 1029.
(9) Burk, P. L.; Osborn, J. A.; Youinou, M.-T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273.
(10) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228.
(11) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, *28*, L121.

0020-1669/84/1323-2459$01.50/0