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Octabromotetraphenylporphyrin and Its Metal Derivatives: Electronic Structure and Electrochemical Properties

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The free-base octabromotetraphenylporphyrin (H_2OBP) has been prepared by a novel bromination reaction of (*meso*-tetraphenylporphyrinato)copper(II). The metal [V^{IV} O, Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Ag(II), Pt(II)] derivatives exhibit interesting electronic spectral features and electrochemical redox properties. The electron-withdrawing bromine substituents at the pyrrole carbons in H_2OBP and M(OBP) derivatives produce remarkable red shifts in the Soret (50 nm) and visible bands (100 nm) of the porphyrin. The low magnitude of protonation constants ($\text{p}K_3 = 2.6$ and $\text{p}K_4 = 1.75$) and the large red-shifted Soret and visible absorption bands make the octabromoporphyrin unique. The effect of electronegative bromine substituents at the peripheral positions of the porphyrin has been quantitatively analyzed by using the four-orbital approach of Gouterman. A comparison of MO parameters of MOBP derivatives with those of the *meso*-substituted tetraphenylporphyrin (M(TPP)) and unsubstituted porphine (M(P)) derivatives provides an explanation for the unusual spectral features. The configuration interaction matrix element of the M(OBP) derivatives is found to be the lowest among the known substituted porphyrins, indicating delocalization of ring charge caused by the increase in conjugation of p orbitals of the bromine onto the ring orbitals. The electron-transfer reactivities of the porphyrins have been dramatically altered by the peripheral bromine substituents, producing large anodic shifts in the ring and metal-centered redox potentials. The increase in anodic shift in the reduction potential of M(OBP)s relative to M(TPP)s is found to be large (550 mV) compared to the shift in the oxidation potential (300 mV). These shifts are interpreted in terms of the resonance and inductive interactions of the bromine substituents.

Introduction

In recent years there has been an increasing interest in the study of high-valent perhalogenated metalloporphyrins for catalytic epoxidation and hydroxylation reactions of organic substrates. The high-valent metalloporphyrin derivatives in the presence of oxygen donors such as PhIO , H_2O_2 , NaOCl , KHSO_5 , or RCOOOH function as efficient catalysts in the epoxidation of organic substrates.¹ The effectiveness of these catalysts has been traced to the stereochemical features of the porphyrins and their stability toward oxidative degradation in the presence of strong oxygen donors. It has been shown that the substitution of electron-withdrawing groups (cyano or bromo) at the pyrrole positions causes an anodic shift in the ring oxidation and reduction potentials of the porphyrins.² The interesting catalytic properties of the halogenated porphyrins offer a scope to study the electronic structure and other features of the metal derivatives of these porphyrins.

The halogen-substituted porphyrins so far reported fall into two classes—halogens appended either at the pyrrole positions³ or at the *meso*-aryl groups⁴ of the porphyrins. The porphyrin that has the halogen substitution both at the pyrrole and *meso*-aryl groups is a tetrakis(2,6-dichlorophenyl)octabromohemin derivative.⁵ The latter compound has been found to be an efficient catalyst in the epoxidation reactions of olefins. Here, we report a novel method of synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenyl-21,23(*H*)-porphyrin (H_2OBP) (Figure 1) through the bromination reaction of (5,10,15,20-tetraphenylporphyrinato)-copper(II) (Cu(TPP)) and its subsequent demetalation by treatment with acid. The electronic spectral and magnetic resonance features of the various V^{IV} O, Co(II), Ni(II), Cu(II), Pd(II), Pt(II), Zn(II), and Ag(II) derivatives of H_2OBP have provided important structural information on these porphyrins. The electrochemical redox behavior of the free-base H_2OBP and its metal derivatives exhibits several interesting features. The

present study illustrates the influence of peripheral bromine substituents on the electronic structure and electrochemical properties of the octabromoporphyrin derivatives.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphyrin (H_2TPP) was prepared according to the method of Rothemund et al.⁶ and purified according to the procedure of Barnett et al.⁷ Copper tetraphenylporphyrin (Cu(TPP)) was synthesized and purified by using reported procedure.⁸ All solvents employed in the present study are of spectral grade and were distilled before use. Liquid bromine procured from Ranbaxy and basic alumina obtained from Acmes were used as received. The metal salts used in the preparation of octabromoporphyrin derivatives are given below. Copper(II) acetate monohydrate, zinc(II) acetate dihydrate, cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, and silver(I) acetate were procured from BDH and used without further purification. Palladium(II) chloride obtained from Ranbaxy was used as received. Dichloro(cyclooctadiene)platinum(II)⁹ and bis(2,4-pentanedionato)oxovanadium(IV)¹⁰ were prepared according to the reported procedures.

Synthesis of 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetraphenylporphyrin (H_2OBP). This was obtained by the bromination reaction of

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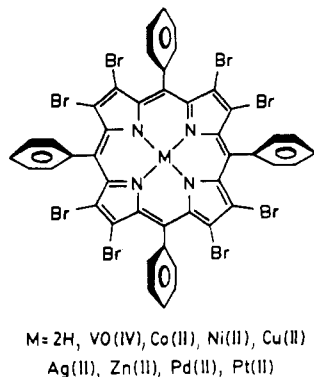


Figure 1. Structure of the free-base octabromotetraphenylporphyrin (H_2OBP) and its metal derivatives ($M(OBP)s$).

CuTPP followed by an acid demetalation reaction. To a stirred solution of Cu(TPP) (0.25 g) in 100 mL of $CHCl_3/CCl_4$ (1:1 v/v) was added 12 mM of liquid bromine in 25 mL of solvent mixture over a period of 30 min at room temperature. The stirring was continued for a further period of 4 h. Pyridine (1.5 mL) in 40 mL of $CHCl_3/CCl_4$ (1:1 v/v) mixture was added dropwise over a period of 30 min. The solution was stirred for another period of 12 h. Then the reaction mixture was treated with 100 mL of 20% aqueous sodium metabisulfite solution to destroy the excess of bromine. The organic layer was separated and dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure to obtain the green product. The product was dissolved in a minimum amount of $CHCl_3$ and chromatographed on a basic alumina column. The first fraction was collected and on evaporation of the solvent yielded 0.37 g (75%) of Cu(OBP).

To a 0.1-g amount of CuOBP in 50 mL of $CHCl_3$ was added 10 mL of perchloric acid (70%). The mixture was stirred for about 8 h. The organic layer was separated, neutralized with 20% aqueous sodium carbonate solution, and dried over anhydrous sodium sulfate. Evaporation of the organic solvent yielded a green residue. This was dissolved in a minimum amount of $CHCl_3$, and the solution was chromatographed on basic alumina to obtain free-base H_2OBP . It was found that the free base obtained in this fashion was contaminated with traces of CuOBP. Analytically pure H_2OBP was obtained by metalation with zinc(II) acetate, and the Zn(OBP) was separated by column chromatography. The details of the synthesis of Zn(OBP) are mentioned separately. Acid demetalation of Zn(OBP) with trifluoroacetic acid followed by neutralization with aqueous sodium bicarbonate yielded analytically pure H_2OBP . 1H NMR (270 MHz) in $CDCl_3$ [position of resonances in ppm (nature of the multiplets, number of protons present in the group)]: 8.21 (m, 8 H, tetraphenyl *o*-H), 7.79 (m, 12 H, tetraphenyl *m*- and *p*-H), -1.65 (bs, 2 H, imino H). Elemental analysis was consistent with porphyrin without solvent of crystallization. Anal. Calcd for $C_{44}H_{22}N_4Br_8$: C, 42.42; H, 1.78; N, 4.49; Br, 51.30. Found: C, 42.35; H, 1.90; N, 4.40; Br, 51.32.

Synthesis of Octabromoporphyrin Derivatives of Metal Ions [$M(OBP)$, $M = Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Ag(II), Pt(II), V^{IV}$]. The metal derivatives of H_2OBP were prepared by using a simplified procedure. A typical procedure for the preparation of (octabromoporphyrinato)zinc(II) is given below.

To H_2OBP (100 mg) in 50 mL of $CHCl_3$ was added zinc(II) acetate (40 mg) in 25 mL of methanol and the reaction mixture stirred for 30 min. At the end of this period the solvent was removed under reduced pressure. The residue thus obtained was dissolved in a minimum amount of chloroform, and the mixture was washed with water to remove excess zinc salt. The chloroform layer was dried over anhydrous sodium sulfate, and the compound was obtained on evaporation of the solvent. The compound was purified by using column chromatography over basic alumina. The yield of the product was found to be 95 mg (90%).

The metal derivatives Co(OBP), Cu(OBP), and Ni(OBP) were prepared with the procedure described above, and the yields are almost quantitative. In the preparation of Ag(OBP) and Pd(OBP), acetic acid was used as a solvent instead of methanol and H_2OBP was taken in chloroform. The purification procedure is the same as described for the preparation of Zn(OBP). The yields of the Ag(OBP) and Pd(OBP) are found to be 85% based on H_2OBP .

Synthesis of (Octabromoporphyrinato)oxovanadium(IV). To H_2OBP (100 mg) in 50 mL of dimethylformamide was added bis(2,4-pentanedionato)oxovanadium(IV) (0.1 g) in 100 mL of dimethylformamide, and the reaction mixture was refluxed for 24 h. The solvent was removed under reduced pressure. The residue was taken in a minimum amount of chloroform and washed with water to remove excess metal salt. The

solution was dried over anhydrous sodium sulfate and column chromatographed on basic alumina with chloroform as an eluant. The first moving fraction was collected and on evaporation of the solvent yielded 85 mg (80%) of the VO(OBP).

The Pt(OBP) derivative was prepared by using the above procedure. Dichloro(cyclooctadiene)platinum(II) (30 mg) was used as a metal carrier. The elemental analysis of all the octabromo derivatives gave satisfactory results in agreement with the elements present in the complexes. 1H NMR (270 MHz) in $CDCl_3$: Ni(OBP), 7.91 (m, 8 H, tetraphenyl *o*-H), 7.70 (m, 12 H, tetraphenyl *m*- and *p*-H); Zn(OBP), 8.12 (m, 8 H, tetraphenyl *o*-H), 7.77 (m, 12 H, tetraphenyl *m*- and *p*-H); Pd(OBP), 8.07 (m, 8 H, tetraphenyl *o*-H), 7.77 (m, 12 H, tetraphenyl *m*- and *p*-H); Pt(OBP), 8.04 (m, 8 H, tetraphenyl *o*-H), 7.75 (m, 12 H, tetraphenyl *m*- and *p*-H); Co(OBP), 15.23 (s, 8 H, tetraphenyl *o*-H), 10.10 (s, 12 H, tetraphenyl *m*- and *p*-H).

Methods. Optical absorption spectra were recorded on an Hitachi U-3400 UV-vis spectrophotometer using a pair of matched quartz cells of 1-cm path length in dichloromethane. The emission spectra were measured on a Perkin-Elmer fluorometer at 77 K in $CHCl_3$ and $CHCl_3/CH_3OH$ glasses.

The protonation constants (pK_3 and pK_4) of H_2OBP were determined by the literature method.¹¹ The change in absorbance of the Soret band (469 nm) of H_2OBP [10^{-5} M solution in $CH_3OH/CHCl_3$ (1:1 v/v)] on increasing addition of trifluoroacetic acid was monitored for the evaluation of protonation constants. The pH values of the solutions were determined by a pH meter using a glass electrode. The response of the electrode had been calibrated earlier. The stability class of the various metal derivatives $M(OBP)$ toward the acid demetalation reaction has been determined by using the method of Buchler.¹²

The cyclic voltammetric measurements of the free-base H_2OBP and its metal derivatives have been carried out on a Bioanalytical System (BAS 100A) instrument comprising an electrochemical analyzer, cell assembly, and videometer. The cell assembly consists of a platinum-button working electrode, a Ag/AgCl reference, and a platinum wire as the auxiliary electrode. Pure dichloromethane was used as solvent. Some of the measurements were made in dimethylformamide, and the potentials were not significantly different from that observed in the case of dichloromethane. The majority of the octabromo derivatives were less soluble in DMF; thus, the values obtained in dichloromethane are given. The concentrations of the free base (H_2OBP) and its metal derivatives were in the range of 1 mM, and tetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte. Solutions were purged with argon gas prior to measurements, and all measurements were made at 296 K. The thin-layer spectroelectrochemical studies were carried out in dichloroethane by using a homemade setup. The thin-layer electrochemical cell consists of an optically transparent gold minigrad as the working electrode, a thin platinum foil auxiliary electrode, and Ag/AgCl as the reference electrode. Electrolyses of the solutions were performed with this cell by using the Model MP-81 Bank Electronic potentiostat. The change in potential during electrolysis was less than ± 10 mV. The performance of the cell was evaluated by using the procedure described by Blubaugh and Doane.¹³

Results

The octabromoporphyrin (H_2OBP) and its metal derivatives ($M(OBP)$) are found to be freely soluble in many organic solvents, and they are stable toward acid. The protonation constants, pK_3 and pK_4 values of H_2OBP determined by the optical absorption method, lie at 2.6 and 1.75, respectively. A comparison of these values with those obtained for the unsubstituted tetraphenylporphyrin (H_2TPP) and porphine (H_2P) indicates that the imino nitrogens of H_2OBP are relatively less basic than those of H_2TPP and H_2P .¹⁴ The acidic nature of H_2OBP possibly arises from the electron-withdrawing substituents (bromine) at the pyrrole carbons. Moreover, the various metal derivatives of H_2OBP are stable toward the acid demetalation reaction and they can be classified according to different stability class. Buchler's stability index values (SI)¹² of the different metal derivatives can be correlated with decrease in stability class as Pd(II), Pt(II), V^{IV} (stability class I) > Ni(II), Cu(II) (stability class II) > Ag(II), Co(II) (stability class III) > Zn(II) (stability class IV).

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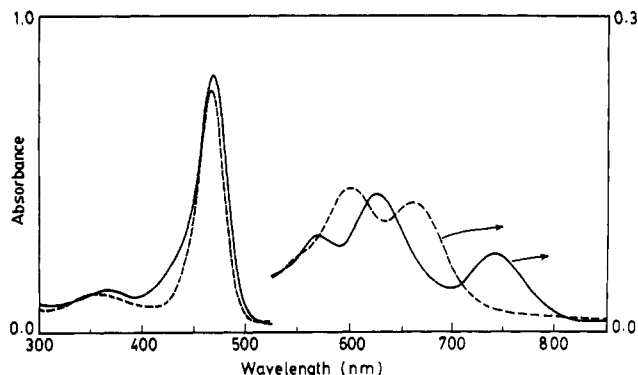


Figure 2. Optical absorption spectra of (a) H₂OBP (—) and (b) Zn(OBP) (---) in CH₂Cl₂ at 296 K. The arrows indicate the absorbance values of the Q bands, and these are depicted on the right ordinate.

The ¹H NMR spectra of H₂OBP and its Zn(II), Ni(II), Pd(II), and Pt(II) derivatives are highly characteristic, and the integrated intensities of the proton resonances are in conformity with the proposed structures. The complete absence of pyrrole proton resonances in the region 8.7–8.9 ppm in the ¹H NMR spectra of the free-base porphyrin and its metal derivatives reveal that all the protons of the pyrrole carbons are substituted with bromine. The proton resonance of the imino hydrogens of H₂OBP occurs in a deshielded region (–1.65 ppm) relative to that observed for the corresponding unsubstituted H₂TTP (–2.75 ppm). The downfield shift of this resonance in H₂OBP indicates decreased electron density of the inner imino nitrogens, a result in accordance with the pK₃ and pK₄ values of H₂OBP. Interestingly, the proton resonances of the ortho, meta, and para protons of the *meso*-aryl groups of Co(OBP) (ortho at –15.23 ppm, meta and para at 10.10 ppm) are considerably deshielded due to the presence of the Co(II) center.¹⁵ A comparison of the resonances with those observed for Co(TPP) is made to isolate any effect induced by the bromine substituents in the porphyrin ring. It is found that the *meso*-aryl proton resonances of Co(OBP) are shifted downfield relative to Co(TPP) (ortho at –13.16 ppm, meta and para at 9.97 ppm), indicating, in addition to the dipolar contributions due to Co(II), there is a decreased π -electron density in the Co(OBP) ring arising from the electron-withdrawing effect of the bromine substituents.

Optical Spectroscopy. The electronic absorption spectra of the free-base H₂OBP and a representative metal derivative Zn(OBP) are shown in Figure 2. The optical absorption spectral data for all the synthesized metal derivatives are given in Table I. It is fruitful to compare the data obtained with those of the unsubstituted porphyrin, 5,10,15,20-tetraphenylporphyrin (H₂TTP), derivatives. This would enable us to bring out the effect of bromine substituents on the electronic spectral features of octabromoporphyrin derivatives. The absorption spectral features of octabromoporphyrin complexes distinctly differ from those of the unsubstituted porphyrin in two respects. The first difference is the energy of the Q and B (Soret) absorption bands, and the second difference lies in the intensity of the Q and B transitions. It may be noted that the free-base H₂OBP in CH₂Cl₂ exhibits three Q bands in contrast to the four-banded spectrum observed for H₂TTP. The origin of the latter lies in the vibronic mixing resulting in the appearance of Q_y(1,0), Q_y(0,0), Q_x(1,0), and Q_x(0,0) transitions in the order of decreasing energy and intensity. The unusually large (fwhm) value of the band at 625 nm suggests a possible overlap of the Q_y(0,0) and Q_x(1,0) transitions in H₂OBP.¹⁶ Interestingly, the B (Soret) and Q band transitions of octabromoporphyrin derivatives show a dramatic shift to the red region relative to the unsubstituted H₂TTP derivatives. Callot³ from the study on the bromination of H₂TTP has pointed out that each bromine substitution at the pyrrole position contributes a shift

Table I. Optical Absorption Spectral Data for Free-Base Octabromoporphyrin H₂OBP and Its Metal Derivatives in CH₂Cl₂ at 296 K^a

compd	B bands, nm	Q bands, nm
H ₂ OBP	370 (4.52), 469 (5.31)	569 (3.96), 626 (4.12), 743 (3.87)
Zn(OBP)	350 (4.62), 466 (5.41)	598 (4.14), 656 (4.09)
Cu(OBP)	365 (4.44), 448 (sh), 466 (5.12)	581 (4.25), 625 (sh)
Ni(OBP)	344 (4.48), 448 (5.39)	561 (4.28), 592 (sh)
Co(OBP)	309 (4.37), 358 (4.36), 446 (5.21)	561 (4.10)
VO(OBP)	362 (4.56), 464 (5.36)	589 (4.25), 627 (sh)
Ag(OBP)	387 (sh), 452 (5.00)	528 (sh), 569 (4.19), 603 (sh), 646 (sh)
Pd(OBP)	315 (4.28), 355 (4.36), 449 (5.3)	514 (3.76), 556 (4.36), 589 (sh)
Pt(OBP)	337 (4.21), 431 (5.18)	539 (4.36), 570 (3.99)
H ₄ OBP ²⁺	426 (4.79), 494 (5.40)	748 (4.76)
OBP ²⁻	328 (4.51), 376 (4.56), 487 (5.36)	735 (4.50)

^a Values in parentheses refer to log ϵ values.

of 6 nm to the red region with respect to the bands observed for H₂TTP. The limiting case in their study was 2,7,12,17-tetrabromo-5,10,15,20-tetraphenylporphyrin. The magnitude of the shifts in the absorption bands obtained in the octabromoporphyrin derivatives are in conformity with this prediction. The oscillator strength (f) of the B and Q transitions of H₂OBP derivatives¹⁷ are generally found to be higher than those observed for H₂TTP (0.01–0.05) derivatives.⁸ All the metal derivatives (M(OBP)) exhibit a band around 350 nm. The origin of this band is similar to that one predicted by Petke et al.¹⁸ in magnesium porphine complexes.

An attempt has been made to rationalize the unusual red shift and enhanced " f " value of the absorption bands of octabromoporphyrin derivatives on the basis of the four-orbital approach of Gouterman.¹⁹ The effect of peripheral substituents on the electronic spectral features of the porphyrins has been discussed in the literature.²⁰ Recently Shelnutt and Ortiz²¹ have advanced a quantitative method of analysis in terms of four-orbital parameters to explain the substituent effects on the π - π^* electronic transitions of metalloporphyrins. The highest occupied molecular orbitals of porphyrins, a_{2u} and a_{1u} , have nodes on the pyrrole carbons and *meso*-carbons, respectively. The presence of substituents on the peripheral positions of the porphyrin is considered as a perturbation leading to multitude of configuration interactions (CI). The nature of the peripheral substituents stabilizes or destabilizes the one-electron excited-state configurations to different extents. The parameters that define the energies of the excited-state molecular orbital configurations are the matrix elements A_{1g} and A'_{1g} , the CI element A''_{1g} , and the ratio of the transition dipoles r/R for one-electron states. An estimate of these parameters is obtained by following the method described in the literature.²¹ Here, an experimental plot of $E_B - E_Q$ versus q_Q^2/q_B^2 (Figure 3) is compared with theoretical curves obtained for assumed values of A''_{1g} and r/R and by varying ϕ .²² The E_B and

(17) The oscillator strengths, f , of the B and Q transitions are determined by using the formula $f = 4.33 \times 10^{-9}(\text{fwhm})\epsilon$, where ϵ is the molar absorption coefficient in mol⁻¹ cm⁻¹ L⁻¹ and fwhm is in cm⁻¹ (Platt, J. R.; Klevens, H. B. *Rev. Mod. Phys.* **1944**, *16*, 182).

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(22) q_Q^2/q_B^2 is the ratio of the square of transition dipoles of the Q and B bands of the porphyrin and related to ϕ by the expression

$$q_Q^2/q_B^2 = \frac{\sin^2 \phi - (r/R) \sin 2\phi + (r/R)^2 \cos^2 \phi}{\cos^2 \phi + (r/R) \sin 2\phi + (r/R)^2 \sin^2 \phi}$$

where $\phi = \frac{1}{2} \tan^{-1} (A_{1g}/A'_{1g})$ (Shelnutt, J. A. *J. Phys. Chem.* **1984**, *88*, 4988.)

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(16) The fwhm value of the band at 625 nm is found to be 2050 cm⁻¹ compared to the average fwhm value (900 cm⁻¹) of the Q band of H₂TTP.

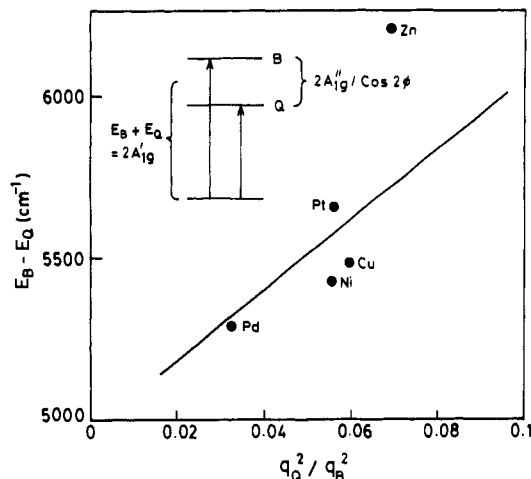


Figure 3. Plot of the difference in energy of the B and Q bands versus the ratio of the dipole strength of the various M(OBP)s. The theoretical plot is shown by a solid line obtained for an assumed value of A''_{1g} and r/R and by varying the ϕ value for each metal derivative. The values of ϕ taken are -14.7 , -13.4 , -12.7 , -9.6 , and 13.5° , respectively, for the Zn(II), Cu(II), Ni(II), Pd(II), and Pt(II) derivatives. A''_{1g} and A'_{1g} are depicted schematically in the inset (see text).

Table II. Energies, Ratios of Dipole Strengths, and Other Parameters for the Metalloporphyrins

metallo-porphyrin	q_Q^2/q_B^2	$E_B - E_Q$, cm^{-1}	$1/2(E_B + E_Q) \times (A'_{1g})$, cm^{-1}	$2A_{1g}$, cm^{-1}	$2A''_{1g}$, cm^{-1}	ref
Zn(OBP)	0.0700	6215	18 328	-2817	5050	a
Cu(OBP)	0.0618	5459	18 729	-2525	5050	a
Ni(OBP)	0.0559	5430	19 606	-2374	5050	a
Pd(OBP)	0.0328	5293	19 624	-1741	5050	a
Pt(OBP)	0.0565	5658	20 372	2547	5050	a
Zn(TPP)	0.0078	6690	20 352	-2107	6335	21
Cu(TPP)	0.0019	6559	20 701	-1720	6335	21
Ni(TPP)	~0	6429	20 990	-890	6335	21
Pt(TPP)	0.0103	6350	21 763	376	6335	21
Zn(P)	0.0157	7205	21 523	20	7190	21
Cu(P)	0.0320	7263	21 814	800	7190	21
Ni(P)	0.0419	7219	22 231	1140	7190	21
Pt(P)	0.0590	7402	22 895	1710	7190	21

^aThis work.

E_Q parameters are respectively the energies of the B and Q bands of the metallooctabromoporphyrins, M(OBP)s, and the transition dipoles of these bands are denoted by q_B and q_Q . The best fit for the experimental curve is obtained when $A''_{1g} = 5050 \text{ cm}^{-1}$, $r/R = 0.01$, and $\phi = -15$ to $+14^\circ$.²³ The considerable deviation of Zn(OBP) in Figure 3 is possibly due to the lowered symmetry of Zn(OBP).²⁴ The values of the various parameters obtained in this study are compared with those observed for M(TPP)s and metal porphyrin (M(P)) complexes (Table II). The choice of the latter (M(P) complexes) for comparison is to bring forth the effect of both meso and pyrrole carbon substitution on the relative magnitudes of the various parameters. The A'_{1g} value represents the average energy of the B and Q transitions, and it is possible to obtain the energy of the $e_g(\pi^*)$ level (LUMO) by assuming that the a_{1u} and a_{2u} levels are degenerate for a hypothetical M(OBP). The A'_{1g}^0 value obtained from the intercept of the plot of A'_{1g} versus $2A_{1g}$ (Figure 4) is found to be $18\,250 \text{ cm}^{-1}$. The

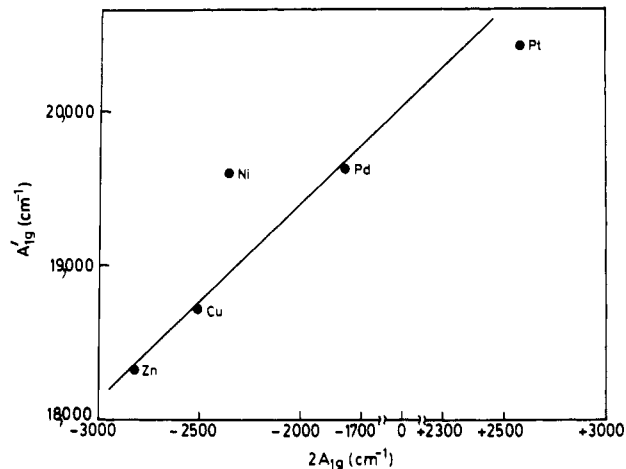


Figure 4. Plot of the average energy of the B and Q transitions (A'_{1g}) versus the energy separation between the a_{1u} and a_{2u} orbitals ($2A_{1g}$) of the different metallooctabromoporphyrin derivatives.

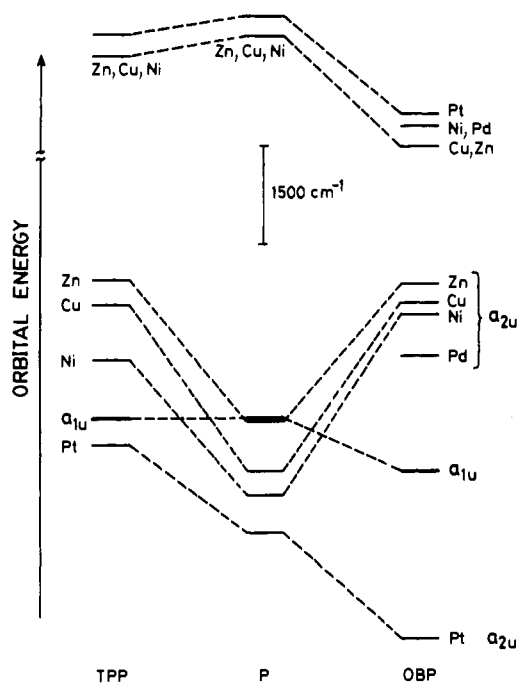


Figure 5. Comparison of energy levels of the molecular orbitals of various metal derivatives of *meso*-tetraphenylporphyrin, H_2TPP , unsubstituted porphyrin, H_2P , and bromine-substituted porphyrin, H_2OBP . The energy of the a_{1u} orbital is calculated from the splitting ($2A_{1g}$) of the Cu(II) derivative. The effects of substitution at the peripheral positions of the porphyrin on the a_{2u} levels are shown. The energy of the a_{2u} orbital in each of the metal derivatives (M(OBP)) is calculated from the MO parameters as explained in the text. The energy of the $e_g(\pi^*)$ orbitals of the M(OBP)s is determined from the A'_{1g} value (Table II), taking into account the contribution from the shift in the a_{1u} level of M(OBP)s relative to M(TPP)s and M(P)s.

relative energies of a_{1u} , a_{2u} , and $e_g(\pi^*)$ for the various M(OBP)s are compared with those of M(TPP)s and M(P)s in Figure 5.

Emission Studies. The emission spectra of free-base H_2OBP and its few metal derivatives have been measured at 77 K in $CHCl_3$ and $CHCl_3/CH_3OH$ (1:1 v/v) glasses. The phosphorescence spectra of H_2OBP and Zn(OBP) consist of three bands at 762, 790, and 825 nm and 728, 765, and 825 nm, respectively, while Ni(OBP) and Cu(OBP) exhibit only two bands at 765 and 825 nm (Figure 6). The excitation spectra obtained at these emissions are identical with the absorption spectra of these derivatives. The triplet lifetimes of H_2OBP and Zn(OBP) measured in $CHCl_3$ at room temperature by using Nd/YAG laser excitation experiments are found to be 113 and 230 ns, respectively. All the phosphorescent bands of the octabromo derivatives are

(23) It may be noted that the slope of the line in Figure 3 is greater than $4A''_{1g}$, indicating the correct choice of r/R value. The intercept of the plot around 5000 cm^{-1} is nearly the same as $2A''_{1g}$.

(24) Recently, we determined the three-dimensional X-ray crystal structure of the zinc(II) derivative of H_2OBP , the salient feature of the structure being that the porphyrin is nonplanar. The Zn(II) ion in the complex has tetragonally elongated octahedral coordination through the four nitrogens of the pyrrole rings in the equatorial plane (Zn-N $\sim 2.01 \text{ \AA}$) and the two nitrogens of the disordered butyronitrile solvent molecules with longer coordination in the axial position (Zn-N $\sim 2.50 \text{ \AA}$).

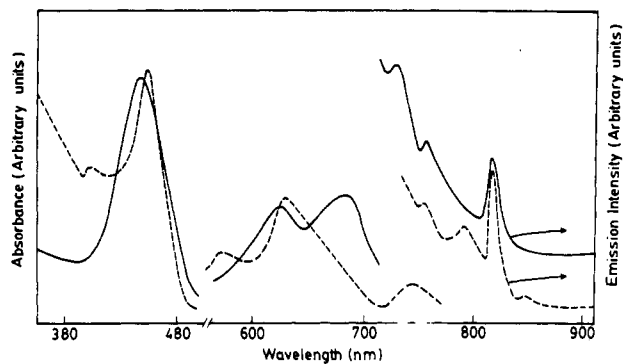


Figure 6. Excitation and emission spectra of H_2OBP (---) in CHCl_3 and Zn(OBP) (—) in a $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:1 v/v) mixture at 77 K. The excitation spectra of the derivatives are shown on the left. The emission spectra of the derivatives are shown on the right in the wavelength region 720–900 nm. The arrows indicate the emission intensity on the right ordinate.

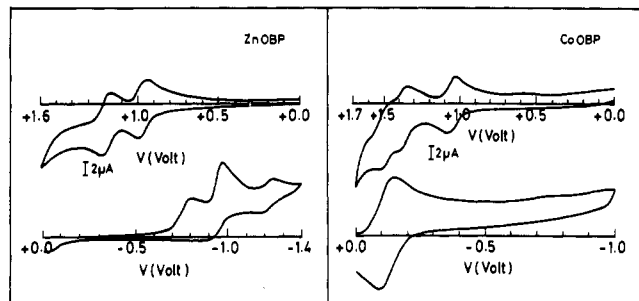


Figure 7. Cyclic voltammograms of Zn(OBP) and Co(OBP) in dichloromethane containing 0.1 M TBAP at 296 K. The concentration of the solution employed is 1 mM.

found to be red shifted and the triplet lifetimes decreased relative to those of the corresponding H_2TPP and Zn(TPP) derivatives. These observations are indicative of an internal heavy-atom effect leading to fast intersystem crossing and resulting in the triplet excited state. Previous studies by Solavev et al.,²⁵ Gouterman and others,²⁶ and Quimby and Longo²⁷ have pointed out that bromine substitution at the *meso*-aryl positions induces an increase in k_{isc} by a factor of about 600 per each bromine substitution although the *meso*-aryl groups are not in direct conjugation with the porphyrin π system. The very large red shift of the phosphorescent bands and diminished lifetime of the triplet excited states of the octabromo derivatives are anticipated, since the bromine substituents are in direct conjugation with the porphyrin π system.

Electrochemistry. Typical voltammograms of the metal derivatives Zn(OBP) and Co(OBP) are illustrated in Figure 7. It is to be noted that the voltammograms of the metal derivatives exhibit characteristic potentials that are reversible, Nernstian, and involve a one-electron process.²⁸ The potentials were calculated as the average of cathodic and anodic peaks. The data are summarized in Table III.

The electrochemical redox behavior of octabromoporphyrin derivatives is similar to that observed for H_2TPP derivatives.²⁹ Thus, the free-base H_2OBP and its metal derivatives exhibit two

Table III. Electrochemical Redox Data^a for Free-Base Octabromoporphyrin H_2OBP and Its Metal Derivatives in CH_2Cl_2 ^b

porphyrin	oxidn		metal redox data	redn	
	$E_{1/2}^I$	$E_{1/2}^{II}$		$E_{1/2}^I$	$E_{1/2}^{II}$
H_2OBP	1.08 ^c	1.70 ^c		-0.56	-0.92
Zn(OBP)	0.96	1.19		-0.93	-1.22
Cu(OBP)	1.18	1.67		-0.59	-0.85
Co(OBP)	1.37	1.51	1.08 (Co(II) = Co(III)) -0.12 (Co(II) = Co(I))		
Ni(OBP)	1.33	2.02		-0.64	-0.95
Pd(OBP)	1.60	1.87		-0.63	-0.91
Pt(OBP)	1.52	1.63		-0.67	-0.98
VO(OBP)	1.43	1.59		-0.49	-0.73
Ag(OBP)	1.73		0.80 (Ag(II) = Ag(III)) -0.09 (Ag(II) = Ag(I))	-1.03	

^aPotentials in volts versus Ag/AgCl . ^bTetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte. The temperature of measurement is at 296 K. ^cPotentials are quasireversible.

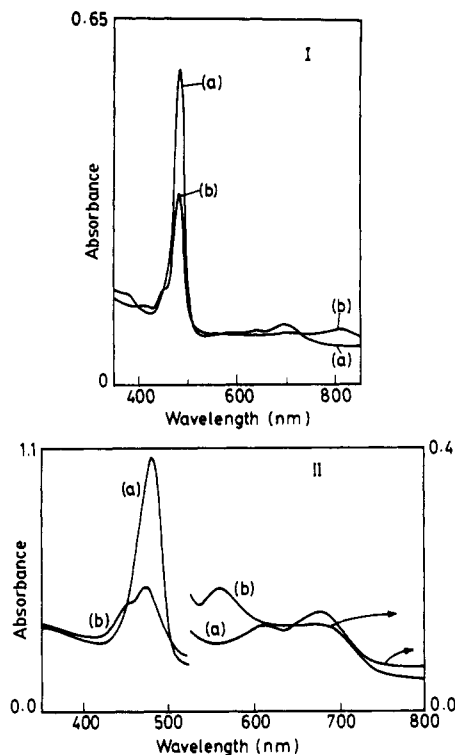


Figure 8. Optical absorption spectra of (I) anion radical $(\text{Zn(OBP)})^{\bullet-}$ and (II) cation radical $(\text{Zn(OBP)})^{\bullet+}$ in dichloroethane produced in a thin-layer spectroelectrochemical cell. (a) and (b) signify respectively the optical absorption spectra of Zn(OBP) before and after electrolysis. The arrows indicate the absorbance scale on the right ordinate. Please note I and II have different scales of wavelength.

oxidation and reduction peaks corresponding to the porphyrin ring oxidation and reduction, respectively. In the case of the Ag(II) and Co(II) derivatives, the first oxidation and reductions are found to originate from the metal center. The most interesting feature is the dramatic change in the magnitudes of the ring and metal-centered oxidation and reduction potentials of octabromoporphyrin derivatives relative to those observed for the corresponding H_2TPP derivatives. It is observed that both ring oxidation and reduction peaks of the octabromoporphyrin derivatives occur at a more positive potential relative to that found for tetraphenylporphyrin derivatives. Interestingly, the anodic shift in the ring reduction potential is more pronounced (550 mV) compared to the shift in the ring oxidation potential (300 mV). This indicates that the presence of electron-withdrawing substituent bromine at the pyrrole carbons makes the porphyrin ring easily reducible and difficult to oxidize relative to the unsubstituted porphyrins. The shift in the potentials are more marked due to pyrrole substitution, while the substitution at the phenyl rings does

- (25) Solavev, K. N.; Tsvirko, M. P.; Gradyshko, A. T.; Kozhich, D. T. *Opt. Spectrosc.* **1971**, 480.
 (26) Gouterman, M.; Khalil, G. E. *J. Mol. Spectrosc.* **1974**, 53, 88. Spallane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, C. Y. *Inorg. Chem.* **1980**, 19, 386.
 (27) Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, 97, 5111.
 (28) The CVs of a few octabromotetraphenylporphyrin derivatives have been measured in DMF though the majority of the derivatives are sparingly soluble in this solvent. We are able to obtain reversible reduction potentials in DMF solvent. The magnitude of the potentials is not significantly different from those reported for CH_2Cl_2 (within the limit +0.1 V).
 (29) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, p 127.

not result in any dramatic shift in the potentials.³⁰ Thin-layer spectroelectrochemical studies have been carried out to characterize the redox products (Figure 8). The one-electron-reduced ($\text{Zn(OBP)}^{\bullet-}$) exhibits an optical absorption not significantly different from that observed for ($\text{Zn(TPP)}^{\bullet-}$)³¹ with a less intense Soret and a long wavelength absorption at 818 nm. The spectrum of the cation radical ($\text{Zn(OBP)}^{\bullet+}$) consists of a split Soret band followed by an absorption band at 550 nm and devoid of any long-wavelength band. This feature is unlike that observed for ($\text{Zn(TPP)}^{\bullet+}$)³² and the reason for this remains unclear.

Discussion

A quantitative understanding of the effects induced by the substituents on the electronic energy levels of M(OBP) s can be obtained from the data given in Table II. The magnitude of the A'_{1g} and A''_{1g} elements of M(OBP) s are decreased relative to those obtained for M(TPP) and M(P) complexes, while an increase in A_{1g} value is observed for different M(OBP) complexes. This suggests that the a_{1u} orbital is stabilized most in M(OBP) s compared to M(TPP) s and M(P) s. It is seen that a_{2u} is destabilized in both *meso*-aryl-substituted M(TPP) and *meso*-aryl- and pyrrole-substituted M(OBP) s, while in the unsubstituted reference M(P) s a_{2u} is stabilized relative to a_{1u} . Moreover, the a_{2u} level is found to be dependent on the nature of the metal ion; the more electronegative metals decrease the energy of a_{2u} , and the less electronegative metals shift the energy of a_{2u} to higher levels. In the case of Pt(OBP) , however, the a_{2u} level is stabilized with respect to a_{1u} similar to that found for the Pt(TPP) complex. This can be ascribed to the interaction of the diffused d orbitals of the third-row transition metal with e_g (π^*) orbitals of the porphyrin.³³ It may be noticed that though a progressive increase in electronegativity of the metal ions in OBP and TPP derivatives shift a_{2u} to lower energy, the overall energy level of a_{2u} in M(OBP) complexes is apparently lower than that observed for M(TPP) complexes. For all the M(OBP) s, a_{1u} remain independent of the nature of the metal ion, since a_{1u} has nodes on the meso carbons.

Another noteworthy point is the magnitude of A''_{1g} and apparent constancy of this value in various M(OBP) s. The value of A''_{1g} (5050 cm^{-1}) is the lowest so far observed among the substituted porphyrins. Since A''_{1g} is the CI matrix element, it is seen that the contribution to CI in M(OBP) complexes is relatively small, indicating decreased electron-electron repulsion. A''_{1g} values for different substituted porphyrins are shown to be linearly dependent on the inductive parameter of the peripheral substituent. It is to be noted that, in a plot of A''_{1g} versus increasing σ values for the various substituted porphyrins, M(OBP) would occupy the lowest point, since σ for bromine is positive and the A''_{1g} value is the least.³⁴ The lower magnitude of A''_{1g} can be rationalized in terms of the conjugation effect induced by the filled p orbitals of bromine substituents at the pyrrole carbons. The electron-withdrawing bromine substituents on the pyrrole carbons would enhance conjugation with the ring, resulting in delocalization of the ring charge and a decrease in electron-electron repulsion and hence the A''_{1g} value. Moreover, the general effect of A''_{1g} is to lower the separation of the B and Q states and to stabilize the e_g (π^*) level. This quantitatively explains the large red shift in the Soret and Q bands.

Among the different substituted porphyrins, octabromoporphyrin is the only known porphyrin that exhibits very large red shift of the Soret and Q bands. It is observed that the Soret and Q bands of the metallooctabromoporphyrins are blue shifted relative to the free-base porphyrin, H_2OBP . The magnitude of the blue shift varies with the nature of the metal ion as $\text{Pt(II)} > \text{Pd(II)}, \text{Ni(II)} > \text{Cu(II)}, \text{Zn(II)}$. An explanation of this feature

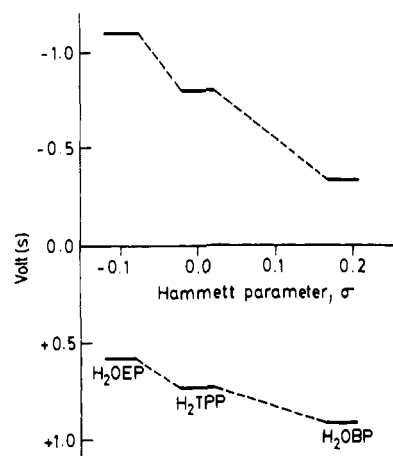


Figure 9. First ring oxidation and reduction potentials (versus SHE) of the different substituted free-base porphyrins plotted against the Hammett parameters (σ) of the substituents. Octaethylporphyrin (H_2OEP), *meso*-tetraphenylporphyrin (H_2TPP) and octabromoporphyrin (H_2OBP) are compared.

lies in the relative destabilization of a_{2u} as a function of the electronegativity of the metal ions. The intensity of the electronic transitions is directly related to the ratio of the matrix elements A_{1g} and A''_{1g} . In view of the low A''_{1g} value, the octabromoporphyrins exhibit fairly intense bands relative to M(TPP) s as a consequence of delocalization of the ring charge.

The electrochemical redox behavior of octabromoporphyrin derivatives provided unusual features. The large (anodic) shift in the ring reduction potential of the octabromoporphyrin derivatives relative to that of unsubstituted porphyrin derivatives is interpreted in terms of increasing resonance interactions of the filled p orbitals of bromine substituents with the π system of the porphyrin. This is supported by the observation of the diminished magnitude of CI matrix element A''_{1g} in M(OBP) derivatives relative to that found in M(TPP) derivatives (Table II). Thus, both inductive and resonance effects govern the relative magnitudes of oxidation and reduction potentials of the octabromo derivatives. It is of interest to note that both metal-centered oxidation and reduction peaks of Ag(OBP) and Co(OBP) are shifted to more anodic potentials relative to that found for the corresponding TPP derivatives. This aspect is examined later.

The differences between the successive ring reduction potentials of the octabromo derivatives are found to be less ($\sim 340 \text{ mV}$) compared to that found for either octaethylporphyrin ($\sim 400 \text{ mV}$) or unsubstituted TPP ($\sim 420 \text{ mV}$) derivatives. This once again emphasizes the resonance contribution induced by the bromine substituents at the pyrrole carbons. It is known that the difference between the first ring oxidation and reduction potentials correlate well with the energy separation between the HOMO and LUMO of the porphyrin derivatives.³⁵ An attempt has been made to depict the difference in the potentials of a few free-base porphyrins in order to bring about the effect induced by pyrrole substituents. Figure 9 illustrates the energy distribution among H_2OEP , H_2TPP , and H_2OBP as a function of increasing Hammett parameter σ values of the substituents. It is seen that the decrease in σ values progressively shifts the ring oxidation and reduction peaks to less anodic potentials. This is rationalized in terms of electron-withdrawing substituents (bromine) at the pyrrole carbons inducing a decrease in the electron density of the conjugated tetrapyrrole system, while electron-donating ethyl groups produce an opposite effect. It is of interest to note that a more general relationship exists between the difference in the first ring oxidation and reduction potentials and the energy of the Q band of the various metal derivatives of octabromoporphyrin derivatives (Figure 10). The linear dependence implies the presence of inductive interactions introduced by the different metal ions. The

(30) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435.

(31) Clack, D. W.; Hush, N. S. *J. Am. Chem. Soc.* **1965**, *87*, 4238.

(32) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451. Felton, R. H.; Dolphin, D.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1969**, *91*, 196.

(33) Buchler, J. W.; Kokisch, W.; Smith, P. D. *Struct. Bonding* **1978**, *34*, 79.

(34) The plot reported here is the Figure 6a in ref 21, where A''_{1g} is plotted against σ for various porphyrins.

(35) Fuhrhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.

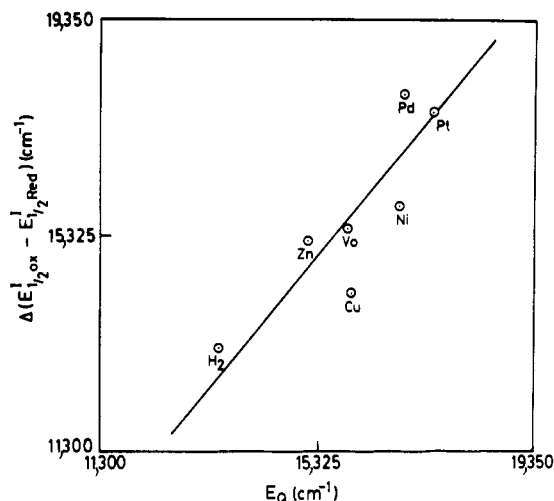


Figure 10. Plot of energy separation between the first ring oxidation and reduction potentials of the different M(OBP)s versus the energy of longest wavelength band of the metalloctabromoporphyrin derivatives.

existence of a σ interaction between the metal ions and the pyrrolic nitrogens is exemplified by the linear dependence of the ring oxidation and reduction potentials with the electronegativity values of the central metal ions in the various metalloctabromoporphyrin derivatives (Figure 11). It is found that the increase in magnitude of the first ring oxidation potentials of M(OBP)s follow the order $\text{Pt(II)} \approx \text{Pd(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)}$, indicating the relative basicity of imino nitrogens in these derivatives. The latter is reflected in the increase in difficulty in acid demetalation as revealed by Buchler's stability class order. It is of interest to note that the electronic structure of the M(OBP)s (Figure 5) reveals that the energy of the highest occupied molecular orbital, a_{2u} (from where the oxidation originates), follows a decreasing order $\text{Pt(II)} > \text{Pd(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)}$. This is in excellent agreement with the experimental observation that the electrochemical oxidation becomes more difficult along the series $\text{Pt(II)} \approx \text{Pd(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)}$ in different M(OBP)s. The metal-centered oxidation and reduction peaks of Co(OBP) and Ag(OBP) occur at a potential less anodic to the corresponding porphyrin ring oxidation and reduction potentials similar to that found in the H_2TPP derivatives. This suggests that the first oxidation and reduction occur from the metal-centered molecular orbital b_{1g} ($d_{x^2-y^2}$) in the case of Ag(OBP) and a_1 (d_{z^2}) in Co(OBP); both these orbitals are situated above the filled a_{2u} orbital of the porphyrin and below the e_g (π^*) orbitals. The relative ease of reduction and difficulty in oxidation of the metal ions in Ag(OBP) and Co(OBP) are related to the electron deficiency of the metal center and electrophilic character of the octabromoporphyrin macrocycle, respectively.

Conclusion

Porphyrins bearing electron-withdrawing bromine substituents at the pyrrole carbons exhibit interesting electronic structure and pronounced effects on the electrochemical redox behavior. The magnitude of the protonation constants of the free-base octabromoporphyrin are the lowest thereby making the most acidic porphyrin among the known substituted *meso*-tetraphenylporphyrins. The bromine substituents produce dramatic shifts

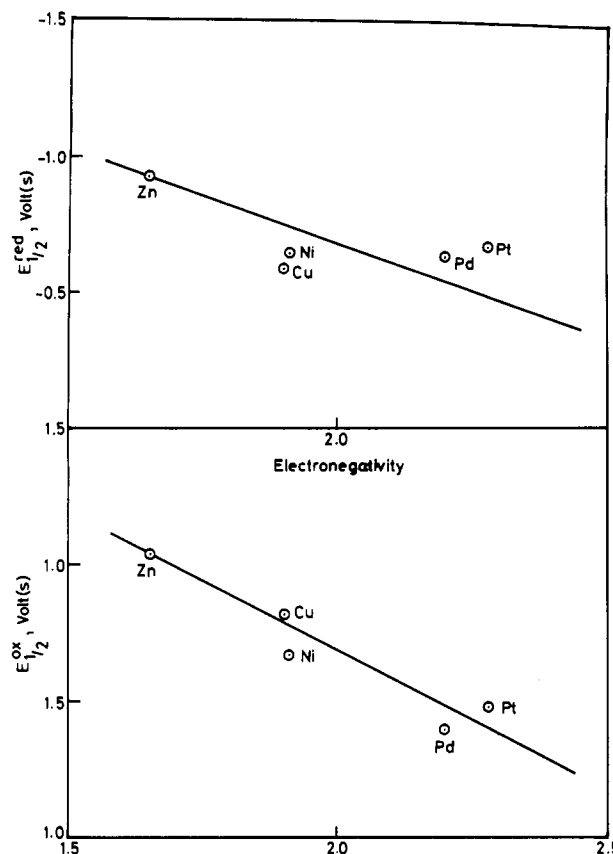


Figure 11. Plot of the first ring oxidation and reduction potentials of the various M(OBP)s versus the electronegativity of the central metal ions. Pauling's electronegativity values of the metal ions are taken.

in the Soret and visible bands of the porphyrins. This has been interpreted in terms of both inductive and conjugative effects induced by the bromine substituents. The low magnitude of the CI matrix element A''_{1g} and the energy separation of a_{1u} and a_{2u} filled π molecular orbitals of the porphyrins are found to be responsible for the red shifts in the absorption bands. Remarkable effects have been observed in the electrochemical redox potentials of the octabromoporphyrin derivatives. The relative ease of reduction and difficulty in oxidation of the H_2OBP derivatives relative to the unsubstituted porphyrin derivatives have been explained on the basis of substituent effects. Excellent correlations are found between the redox potentials, orbital energies, electronic absorption bands, and the intensity of the transitions of the octabromoporphyrin derivatives. The relatively high oxidation potentials and the low basicity of the octabromoporphyrins provide a rational explanation for the stability of these derivatives toward oxidative degradation.

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