

sis has demonstrated that fusing the chelated linear tetramine ligand with an ethylene group generally imposes on the existing chelated rings the extra potential energies more in terms of the nonbonded repulsion and the angular strain than in terms of the bond length and the torsion, and that the *RS* (or *SR*) structure having more nonbonded interactions and angle deformations than the *RR* (or *SS*) form^{13,19} is subjected to more configurational and conformational changes compared with the latter.

The angular strain around cobalt atom is seen to increase at the two bond angle bendings as ethylene bridges in tetramine ligands increase (Figure 7). The strain-free tetraammine geometry adopts an undistorted octahedron. Addition of an ethylene bridge to a slightly distorted bis(ethylenediamine) complex forms two diastereomeric trien isomers: β -*RR* (or *SS*) with less strain and β -*RS* (or *SR*) with more strain. A further ethylene bridging yields the cyclic 12-membered ring with even more angular distortions around the cobalt atom. This very qualitative picture might account partially for the increasing visible absorption intensities as one goes from *cis*-[Co(NH₃)₄X₂]⁺ to *cis*-[Co(en)₂X₂]⁺, *cis*- β -*RR*-[Co(trien)X₂]⁺,

cis- β -*RS*-[Co(trien)X₂]⁺, and finally to *cis*-[Co(cyclen)X₂]⁺.^{4,19,35,36}

Acknowledgment. We thank Dr. Y. Kushi of Hiroshima University for a very valuable discussion.

Registry No. [Co(cyclen)(NO₂)₂]Cl, 15654-24-7.

Supplementary Material Available. Table II, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2886.

(35) In view of the close similarities to β -trien geometries which are known to have rigid conformations¹⁶ it is concluded that the conformation of the cyclen complex in solution is close to that found in the solid state.

(36) In correspondence with the gradual expansion of the N-Co-N angle, the X-Co-X angle becomes narrower: *cis*-[Co(en)₂X₂]⁺ (90°),³¹ racemic β -*RR*- and/or *SS*-[Co(trien)Cl(H₂O)]²⁺ (88.6°),¹⁵ *cis*- β -*RS*-[Co(dimetrien)(NO₂)₂]⁺ (86.3°),²⁸ and *cis*-[Co(cyclen)(NO₂)₂]⁺ (84.5°).

Contribution from the National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo, Japan, and from the Department of Chemistry, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo, Japan

X-Ray Photoelectron Spectroscopy of Azaporphyrins

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The X-ray photoelectron spectra of azaporphyrins were studied. The nitrogen 1s spectra of the free bases revealed that each inner proton is localized on one of the central nitrogens even if the meso methine bridges in porphyrins are substituted by aza nitrogens. An intramolecular hydrogen-bonding interaction between the meso-bridging aza nitrogen and the inner proton is quite impossible. In the metal complexes, the central and meso-bridging nitrogens are close in their charge density. With an increase in the number of aza substitutions in the meso bridge, the net electron donation from ligand to metal decreases and thus the metal positive charge increases. The shifts of nitrogen 1s and metal 2p_{3/2} binding energies in azaporphyrins are attributed to an electron-withdrawing effect by meso-bridging nitrogens but not to a contraction of the hole in molecular center. For a given ligand, the nitrogen 1s binding energy varies slightly with metals but the carbon 1s spectra of the metal complexes are essentially the same in their profile and position as the spectrum of the free base. The observations were explained by an extended Huckel molecular orbital calculation.

Introduction

The location of free-base protons in metal-free porphines has been the subject of long debate. Proposed structures are (a) two pyrrole and two aza groups (bonded structure), (b) shared protons (bridged structure), and (c) hydrogen-bonded models somewhere between. It is clear from various studies that the central protons are localized on a diagonally opposed pair of nitrogens in porphyrin free bases. However, the position of central protons in phthalocyanine free base (H₂Pc) is still a matter of controversy.²

By X-ray photoelectron spectroscopy, we showed evidences for the bonded structure of H₂Pc and tetraphenylporphine free base (H₂TPP).³ Zeller and Hayes (Z-H) also concluded the bonded structure of H₂TPP; however, they could not draw a definite conclusion from their broad unresolved N 1s

photoelectron peak of H₂Pc.⁴ Z-H suggested that an intramolecular hydrogen bonding prevents the resolution of distinct N 1s peaks in H₂Pc.

The authors who concluded the bridged structure of H₂Pc emphasized the presence of meso-bridging aza nitrogens.⁵⁻⁷ The lone pair of the meso-bridging nitrogens in H₂Pc is equally effective in attracting protons as that of the inner nitrogens and thus an inner proton forms hydrogen bonds between two inner and one bridge nitrogens, while the lack of meso-bridging nitrogens in porphine leaves the inner proton localized on one of the central nitrogens.

One object of the present work is to elucidate the effect of meso-bridging aza nitrogens on the location of the inner protons. For this purpose, we measured the N 1s photoelectron spectra of tetrabenzmonoazaporphine free base (H₂-TBMAP) and tetrabenztriazaporphine free base (H₂TBTAP)

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(2) Reviews are found in the following references: Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974); A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta*, **25**, 62 (1972).

(3) Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974).

(4) M. V. Zeller and R. G. Hayes, *J. Amer. Chem. Soc.*, **95**, 3855 (1973).

(5) B. D. Berezin, *Russ. J. Phys. Chem.*, **39**, 165 (1965).

(6) I. Chen, *J. Mol. Spectrosc.*, **23**, 131 (1967).

(7) E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).

in which the meso methine bridges of tetrabenzporphine free base are partially substituted by aza nitrogens.

The naturally occurring porphyrins are found in the metal ion incorporated states. The electronic structures of metalloporphyrins have been extensively studied using various experimental techniques. The X-ray photoelectron spectroscopy can offer further information related to charge distribution.^{8,9} In the present study, the C 1s, N 1s and metal $2p_{3/2}$ photoelectron spectra were measured on the tetraphenylporphine and phthalocyanine complexes of various first-row transition metals together with CuTBMAP and CuTBTAP with the intention of studying (a) the charge distributions in porphyrins and azaporphyrins and (b) the effect of meso aza substitutions to the metal-ligand bonding.

There have been many theoretical studies on porphyrins and phthalocyanines by molecular orbital calculations in various degrees of sophistication. The Pariser-Parr-Pople self-consistent molecular orbital theory reproduced the spectroscopic characters quite satisfactorily.¹⁰ However, the π -electron approximation is incapable of describing whole metal-ligand interactions. The metal-ligand interaction can be taken into account explicitly in the extended Huckel molecular orbital (EHMO) calculations, although the method includes electronic interactions rather indirectly. Kramer and Klein found a good correlation between measured Fe 3p binding energies and the iron atomic charges obtained by the EHMO method for various iron compounds including FeClPc.¹¹ Gouterman and coworkers have carried out systematic studies on the electronic structures of porphyrins and related compounds by means of the EHMO calculations.¹² The observations in the present study are well interpreted on the basis of the similar calculations.

Experimental Section

All phthalocyanines studied were obtained from Eastman Kodak Co. and purified by sublimation under vacuum. The other compounds were synthesized and purified by the methods in the literature and identified by chemical analysis.^{13,14}

X-Ray photoelectron spectra were measured on a Varian IEE-15 photoelectron spectrometer using Mg K α radiation. On this spectrometer, the instrumental contribution to line width is kept constant throughout the entire spectrum. Under the experimental conditions employed in the present measurement, the full widths at half-maximum (FWHM) of both C 1s and N 1s photopeaks originated from the corresponding atoms in a chemical environment have been found to be about 1.1 eV in our other observations.

All the samples were sublimed under vacuum directly onto a copper sample holder as a thin film so as to bring the samples into good electrical contact with the spectrometer.

For all the samples, an intense C 1s photopeak observed in the

lowest energy side, whose FWHM was nearly 1.1 eV, was used as a standard for binding energy. As discussed later, the peak arises from the carbon atoms of aromatic hydrocarbon character in the compounds. The binding energy at the peak was assumed constant for all the compounds. The binding energy at the standard peak was determined to be 284.8 eV such that it could reproduce the binding energies of N 1s electrons obtained for various nitrogen compounds.^{8,15} In the following, the photoelectron spectra are compared in binding energy but not kinetic energy.

The overlapping peaks were deconvoluted on a Varian 620-i digital computer. A straight line connecting two points of the observed background on both sides of a band was regarded as the base line. The observed spectrum subtracted by the background contribution was reproduced by a superposition of gaussians with FWHM of about 1.1 eV. The parameters to be determined were the line position and height for each composite peak. An optimum set of the parameters was obtained in such a way that the root-mean-square deviation of the trial spectrum was minimized by changing the parameters according to the simplex method for function minimization.¹⁶

Calculations

The charge densities were calculated by the extended Huckel molecular orbital method. The overlap integrals S_{ij} were evaluated using the Slater atomic orbitals i and j and the Coulomb integrals H_{ii} were estimated from the valence-state ionization potentials assuming their linear dependence on the atomic charge q_i . The data of the valence-state ionization potentials were set as the same as those of Gouterman and his coworkers.¹² The resonance integrals H_{ij} were approximated by the Wolfsberg-Helmholz relation.¹⁷ The atomic charges were obtained by the Mulliken population analysis.¹⁸ At each iteration, the H_{ii} values were obtained from those of the previous cycle employing a damping parameter of 0.1. Iterations were continued until the atomic charges reproduced within 0.01 electronic charge. An intramolecular Madelung potential at atom i was calculated by the formula $\sum_{j \neq i} q_j / r_{ij}$ where q_j is the calculated charge on atom j , r_{ij} is the distance between atoms i and j , and the summation extends over all the atoms except i . The molecular geometries used in the calculations were obtained from X-ray crystallographic data.¹⁹⁻²¹

Results and Discussion

Two C 1s peaks with FWHM of 1.1 eV are observed for H₂Pc and CuPc, while a rather broad C 1s peak with FWHM of 1.3 eV is observed for H₂TPP and CuTPP. In the case of phthalocyanine, the intense peak of lower binding energy is assigned to 24 carbon atoms of aromatic hydrocarbon character and the second peak of intermediate intensity is assigned to eight carbon atoms bonding with two nitrogen atoms.³ In the case of tetraphenylporphine, however, the C 1s peaks of the aromatic carbons and the carbons bonding with a nitrogen are not detected as separate peaks because of their small difference in 1s binding energy. Tetrabenztri-azaporphyrins exhibit a similar profile to the C 1s spectrum of phthalocyanine and tetrabenzmonoazaporphyrins show a similar spectrum to that of tetraphenylporphine. For a variety of the number of meso-bridging aza nitrogens, the

(8) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967.

(9) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

(10) C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectrosc.*, **16**, 415 (1965); A. J. McHugh, M. Gouterman, and C. Weiss, *Theor. Chim. Acta.*, **24**, 346 (1972).

(11) L. N. Kramer and M. P. Klein, *Chem. Phys. Lett.*, **8**, 183 (1971).

(12) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966); **8**, 26 (1967); *Inorg. Chem.*, **5**, 1699, 1707 (1966); M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966); A. M. Schaffer and M. Gouterman, *ibid.*, **18**, 1 (1970); *ibid.*, **25**, 62 (1972).

(13) P. Rothenmund and A. R. Menotti, *J. Amer. Chem. Soc.*, **70**, 1808 (1948).

(14) P. A. Barrett, R. P. Linstead, and G. A. P. Tvey, *J. Chem. Soc.*, 1809 (1939); P. A. Barrett, R. P. Linstead, F. G. Rundall, and G. A. P. Tvey, *ibid.*, 1079 (1940).

(15) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

(16) J. A. Nelder and R. Mead, *Comput. J.*, **7**, 308 (1965).

(17) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(18) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(19) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Amer. Chem. Soc.*, **85**, 2334 (1963).

(20) E. B. Fleisher, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, **86**, 2342 (1964).

(21) C. J. Brown, *J. Chem. Soc. A*, 2488 (1968).

Table I. Charges on Nitrogen and Carbon Atoms in the Typical Porphine Obtained by the Extended Huckel Molecular Orbital Calculations

	N	C _α ^b	C _β ^c	C _m ^d
H ₂ P ^a	-0.10 (pyrrole) -0.31 (aza)	0.02	-0.06	-0.03
CoP	-0.20	0.02	-0.05	-0.03
CuP	-0.20	0.02	-0.05	-0.02
ZnP	-0.20	0.02	-0.05	-0.03

^a Porphine is abbreviated to P. ^b α carbon in pyrrole ring. ^c β carbon in pyrrole ring. ^d Meso methine carbon.

relative intensities of the C 1s peaks increase in proportion to the numbers of the corresponding carbon atoms involved. This indicates that the C 1s peak of the lowest binding energy arises from the carbons of aromatic character but not from some instrumental contaminations. Under the experimental conditions employed in the present work, the C 1s spectra could be reproduced even when the deposit of the contaminant was encouraged by cooling the samples with liquid nitrogen.

The C 1s photoelectron spectra of H₂TPP and H₂Pc were previously explained by the noniterative EHMO method.³ In H₂Pc, a high charge density is predicted on the carbons bonding with two nitrogens and almost neutral charges are predicted on the other carbons. In H₂TPP, a small positive charge appears on the carbons bonding with a nitrogen and almost neutral charges appear on the other carbons. The iterative calculations in the present work also yielded similar results. The C 1s spectra of the complexes of various first-row transition metals were essentially the same in profile and position as that of the free base. Table I lists the charge densities obtained for typical porphines. In accordance with the observations, the calculated charge on carbon atoms in a given ligand does not vary regardless of metal complexes or metal-free base. The interaction of metal and ligand orbitals causes only a little effect in the population on carbons. This justifies our energy-standardization procedure.

As shown in Figures 1 and 2, two resolved peaks were observed in the N 1s spectra of H₂TBMAP and H₂TBTAP, indicating the presence of at least two kinds of nitrogens in each molecule. The observed binding energies of the N 1s peaks are shown in Table II. The energy separation between two N 1s peaks (ΔE_{N1s}) and the observed relative intensity (I_{obsd}) of the higher binding energy peak to the lower binding energy peak are presented in Table III together with the values obtained for H₂TPP and H₂Pc.³

H₂TBMAP and H₂TBTAP have one and three aza nitrogens, respectively, at the meso positions. In the bonded structure there are two kinds of nitrogens in the central part, namely, two pyrrole and two aza nitrogens, while in the bridged structure there are four equivalent porphinato nitrogens sharing protons. The central aza and meso-bridging aza nitrogens in the bonded structure are so close in their 1s binding energy that they do not give rise to two separate peaks but only a single peak. In both structures, the 1s binding energy of the nitrogens bonding with hydrogen should be greater than those of aza nitrogens. Thus, in principle, two N 1s peaks are expected. However, a separation between these peaks should be large only in the bonded structure. The ΔE_{N1s} obtained for H₂TBMAP and H₂TBTAP was comparable to those observed for H₂TPP and H₂Pc. The relative intensities expected from the numbers of different nitrogens in both structures, I_{bond} and I_{bridge} , are presented in Table III. It is obvious that the bonded structure is quite possible for H₂TBMAP and H₂TBTAP as well as H₂TPP and

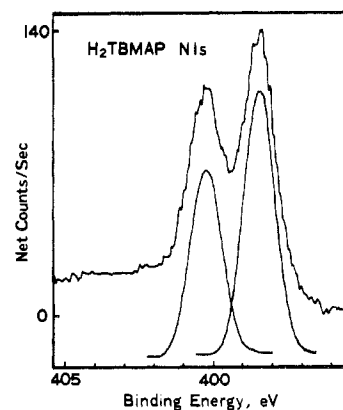


Figure 1. Nitrogen 1s photoelectron spectrum of H₂TBMAP using Mg K α radiation. The binding energy scale was corrected assuming the binding energy of the lowest binding energy carbon 1s peak to be 284.8 eV. The spectrum was deconvoluted into superposing two gaussians with FWHM of 1.1 eV as shown in the bottom.

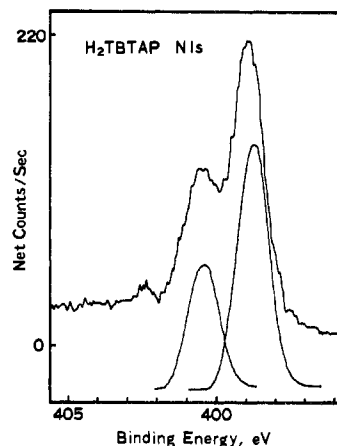


Figure 2. Nitrogen 1s photoelectron spectrum of H₂TBTAP using Mg K α radiation. The binding energy scale was corrected assuming the binding energy of the lowest binding energy carbon 1s peak to be 284.8 eV. The spectrum was deconvoluted into superposing two gaussians with FWHM of 1.1 eV as shown in the bottom.

Table II. Observed Binding Energies (eV) of the Nitrogen 1s Peaks

H ₂ TPP ^a	398.2 (398.2) ^b	H ₂ Pc ^a	398.9 (398.9)
	400.2 (400.1)		400.4
CoTPP	398.8 (398.2)	TiOPc	399.1
CuTPP ^a	398.9	VOpc	399.1
ZnTPP	398.6 (398.2)	MnPC	399.2
H ₂ TBMAP	398.3	FePc	399.2
	400.1	CoPc	399.3
CuTBMAP	399.0	NiPc	399.3
H ₂ TBTAP	398.9	CuPc ^a	399.2 (398.5)
	400.5	ZnPc	399.0
CuTBTAP	399.1		

^a The data of the previous study.³ ^b The values given in the parentheses are the data of Zeller and Hayes,⁴ which were adjusted such that the binding energy of aza nitrogens in H₂TPP fits with ours.

H₂Pc, although I_{obsd} 's were constantly about 0.1 larger than I_{bond} 's.

A small deviation of I_{obsd} and I_{bond} is attributed to a satellite peak, with which the N 1s peak of lower binding energy is accompanied, overlapping with the N 1s peak of higher binding energy. A weak peak of the highest binding energy in the N 1s spectrum of H₂TBTAP is assigned to a satellite of the N 1s peak of higher binding energy. Such a peak, however, was not detected for H₂TBMAP because of the low signal-to-noise ratio for the satellite peak in the experimental conditions. Even if it was so, a satellite of the

Table III. Energy Separations and Relative Intensities of Two Nitrogen 1s Peaks for the Free Bases

	n^a	$\Delta E_{N_{1s}}^b$ eV	I_{obsd}^c	I_{bond}^d	I_{bridge}^e
H ₂ TPP ^f	0	2.0	1.12	1.00	Single peak
H ₂ TBMAP	1	1.8	0.78	0.67	4.00
H ₂ TBTAP	3	1.6	0.52	0.40	1.33
H ₂ Pc ^f	4	1.5	0.40	0.33	1.00

^a The number of meso-bridging aza nitrogen atoms in the ligand.

^b The difference in binding energy between two nitrogen 1s peaks.

^c The observed relative intensity of the higher binding energy peak to the lower binding energy peak. ^d The relative intensity expected from the number of pyrrole and aza nitrogen atoms in the bonded structure. ^e The relative intensity expected for the bridged structure.

^f The data of the previous study.³

N 1s peak of lower binding energy might be present since a difference between I_{obsd} and I_{bond} is comparable to the relative intensity of a satellite to its parent peak observed in similar compounds such as H₂TPP, H₂Pc, and their metal complexes.

The observations in the present work reveal that all the free bases are most likely of bonded structure and the possibility of the bridged structure is excluded. The N 1s peak of higher binding energy is assigned to pyrrole nitrogens and that of lower binding energy is assigned to aza nitrogens. The EHMO calculations predict that the charge on pyrrole nitrogens becomes more negative when the N-H bond of pyrrole is elongated by a hydrogen-bonding interaction with meso-bridging aza nitrogens.³ If it is the case, the 1s binding energy of the pyrrole nitrogens should become lower than otherwise. Such an interaction gives rise to a variation in binding energy for different aza nitrogens and thus a broadening of the N 1s peak of lower binding energy. All the aza-porphyrin free bases studied, however, showed neither such a shift toward lower energy of the 1s binding energy of pyrrole nitrogens nor a broadening of the 1s peak of aza nitrogens. Thus a possibility of the intramolecular hydrogen-bonding interaction of pyrrole with meso-bridging aza nitrogens can be ruled out. With an increase in the number of aza substitutions in the meso bridges, the observed 1s binding energies of both pyrrole and aza nitrogens increase while the $\Delta E_{N_{1s}}$ decreases as shown in Table III. This implies that an increase in the number of meso-bridging aza nitrogens results in reductions of the charge density on the central nitrogens and of the difference in populations on various nitrogens. The EHMO also predicts that the meso nitrogens withdraw electrons from the central pyrrole and aza nitrogens through the conjugated system.

The binding energies of the N 1s peak observed for various metal complexes are presented in Table II with those obtained for CuTPP and CuPc.³ The N 1s spectra of CuTBMAP and CuTBTAP are very similar to those of CuTPP and CuPc, respectively. In the N 1s spectra of all the metal complexes studied, a single sharp peak was observed between two strong N 1s peaks of the related free base. In addition, a weak peak was observed at higher binding energy. This peak was assigned to a satellite peak with which the N 1s peak is accompanied. Such a satellite peak was found also in the C 1s spectra.

The FWHM of 1.1 eV was obtained in the case of metallo-tetraphenylporphyrins with four equivalent nitrogens. A single peak with FWHM of 1.1 eV was observed also for metallophthalocyanines, CuTBMAP and CuTBTAP, in which two kinds of nitrogens, namely, central nitrogens donating to central metal ion and meso-bridging aza nitrogens, are present. This indicates quite a small difference present in the atomic charges of nonequivalent nitrogens involved.^{3,4}

Table IV. Calculated Atomic Charges and Intramolecular Madelung Potentials on the Nitrogen Atoms in Phthalocyanines

	Nitrogen	Charge	Madelung potential, eV
H ₂ Pc	Pyrrole	-0.05	3.32
	Aza	-0.25	2.22
	Bridge	-0.20	1.63
MnPc	Center	-0.13	0.51
	Bridge	-0.18	1.13
FePc	Center	-0.12	0.86
	Bridge	-0.20	1.28
CoPc	Center	-0.15	1.31
	Bridge	-0.18	1.24
NiPc	Center	-0.15	1.14
	Bridge	-0.19	1.23
CuPc	Center	-0.15	1.23
	Bridge	-0.20	1.27
ZnPc	Center	-0.15	1.80
	Bridge	-0.20	1.50

Table IV lists the calculated charges on different kinds of nitrogens in phthalocyanines. As seen in the table, the central nitrogens of metallophthalocyanines are less negative than the meso-bridging aza nitrogens, while the central aza nitrogens in H₂Pc are more negative than the meso-bridging aza nitrogens. The difference in charges calculated for these nitrogens ranges from 0.03 to 0.08 e. This may be sufficient for a broadening of the N 1s peak even if two resolved peaks cannot be observed. In fact a difference in calculated charges between the pyrrole and aza nitrogens in porphine free base is 0.21 e (Table I), which corresponds to a splitting in N 1s binding energy of 2.0 eV observed for H₂TPP.

An intramolecular Madelung potential compensates the effects arising from the presence of nitrogen atoms with different charges.^{8,9} The calculated intramolecular potentials at different nitrogens are shown in Table IV. The potential reduces a difference in the N 1s energies of different nitrogens. Any attempt to include this term, however, gave no improvement in the correlation between observed N 1s binding energies and calculated nitrogen charges. The intermolecular Madelung potential also does not make any important contribution to the binding energy because no crucial electrovalences are present between phthalocyanine molecules as has been shown in X-ray studies of CuPc²¹ and NiPc.²²

The observed energy levels of N 1s and metal 2p_{3/2} electrons are illustrated in Figure 3 for the free bases and their metal complexes. The 1s binding energy of nitrogens in metal complexes was higher than that of aza nitrogens in the corresponding free base but lower than that of pyrrole nitrogens. This shift in N 1s binding energy implies that a charge transfer from nitrogen to metal upon metal complex formation reduces the electron density on the central nitrogen but to less extent than a mean of the aza and pyrrole nitrogens of the free base. For a given metal, the electron density on the central nitrogens decreases in aza substitution in the meso-bridge position. This is ascribed to an electron-withdrawing effect of the meso-bridging aza nitrogens. For a given ligand, however, the N 1s binding energy varies slightly with the central metals.

The EHMO calculation predicts a change in the charges on nitrogens upon metal complex formation but only a small variation with metals (Tables I and IV). The observed N 1s binding energies are plotted against the calculated nitrogen charges as in Figure 4.

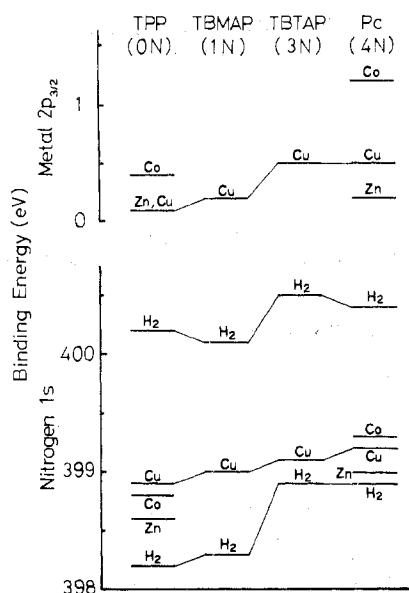


Figure 3. Binding energy diagram of the nitrogen 1s and metal $2p_{3/2}$ electrons. The number of meso-bridging aza nitrogen atoms is indicated in the parentheses. The metal $2p_{3/2}$ binding energies are the relative values. The zero energies for cobalt, copper, and zinc atoms are 780, 935, and 1022 eV, respectively.

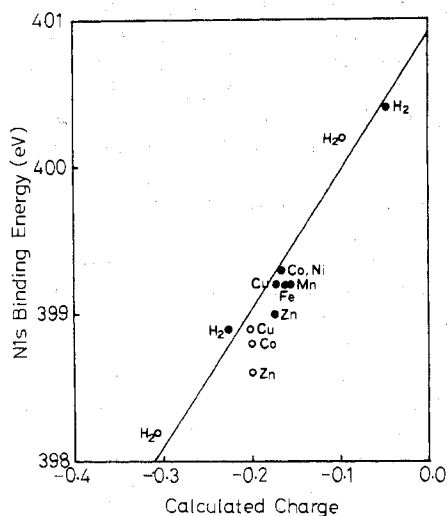


Figure 4. Plots of the observed nitrogen 1s binding energies vs. the nitrogen atomic charges calculated by the extended Huckel molecular orbital method. The open circles indicate tetraphenylporphyrins and the solid circles indicate phthalocyanines. The calculated charges on nitrogens in metallophthalocyanines and on aza nitrogens in H_2Pc indicate an average of the calculated charges on the central and meso-bridging aza nitrogens and of those on the central aza and meso-bridging aza nitrogens, respectively.

The central metal atom becomes less positive as the charge transfer of ligand to metal increases. As seen in Figure 3, metal $2p_{3/2}$ binding energy increases with an increase in the number of meso-bridging aza substitutions, although only a small shift was observed in Zn $2p_{3/2}$ binding energy. The metal charge in a metallophthalocyanine is greater than that of the corresponding metallotetraphenylporphyrin and their difference becomes appreciable in cobalt. The measured binding energies of metal $2p_{3/2}$ peaks and the calculated atomic charges on metal are presented in Table V. The EHMO calculation also predicts a greater metal charge in metallophthalocyanines than that of the corresponding metalloporphyrin. An experimental observation shows that a one-electron attachment to a metal ion in tetraphenylpor-

Table V. Observed Metal $2p_{3/2}$ Binding Energies and Calculated Atomic Charges on the Metal

Metal	Binding energy, eV		Atomic charge	
	TPP	Pc	P	Pc
Co	780.4	781.2	0.31 (0.31) ^a	0.34
Cu	935.1	935.5	0.26 (0.28)	0.31
Zn	1022.1	1022.2	0.40 (0.42)	0.48

^a The values given in the parentheses are the charges obtained for a geometry with a contracted hole as in phthalocyanine.

phines and phthalocyanines causes a chemical shift of about 2 eV in the $2p_{3/2}$ peak of cobalt and copper.²³ Thus the calculated difference in the metal charges seems smaller than expected from the observed shifts.

The molecular geometry may also be responsible for the shifts in N 1s and metal $2p_{3/2}$ binding energies. The radius of the central hole in phthalocyanines is about 0.05 Å smaller than that of porphyrins.⁷ The MO calculations using a geometry with a contracted hole as in phthalocyanines, however, result in no appreciable change in the nitrogen charges and a slight increase in the central metal charge (indicated in the parentheses in Table V). Thus a smaller charge transfer and a higher positive charge on metal in phthalocyanines predicted by the photoelectron spectrum is attributed to an electron-withdrawing effect of the meso-bridging aza nitrogens.

The N 1s binding energies obtained by Z-H⁴ are also given in Table II. The data were adjusted on a scale such that their binding energy of aza nitrogens in H_2TPP fits with ours. A discrepancy of 0.4–0.7 eV is beyond the experimental error. According to the results of Z-H, the 1s binding energies of nitrogens in CoTPP and ZnTPP are not so different from that of aza nitrogens in H_2TPP . In the present work, we never experienced such a singular difficulty in getting reproducible spectra as reported by Z-H. All the photoelectron spectra we obtained were well reproduced in binding energy and intensity. The average binding energies were reproduced within 0.1 eV by at least four runs on a sample. This is better than the value of Z-H (0.2 eV). Z-H observed only a broad unresolved N 1s peak for H_2Pc .⁴ However we could observe two distinct N 1s peaks for H_2Pc and determine their binding energies.³ Z-H mounted the powdered sample on a piece of double-sided Scotch tape attached to an aluminum sample holder and standardized the binding energy with reference to that of a thin gold layer evaporated over the sample. Obviously their procedure gives a less uniform sample surface and results in a greater sample charging during X-ray irradiation than ours. Such a heterogeneous charging over the sample surface gives rise to a broadening of photoelectron peaks and affords only poor reproducibility in measurements of binding energies.

Sublimed gold has been widely used as a calibrant for X-ray photoelectron spectroscopy.²⁴ Betteridge, Carver, and Hercules, however, have observed that gold can react with a number of samples giving rise to chemical shifts of Au 4f peaks to either higher or lower binding energies.²⁵ In their measurements, the Au 4f spectrum of gold evaporated on a CuPc surface showed a complicated structure which depends on the probe temperature and the amount of gold deposited. Thus the gold no longer can serve as a reliable calibrant for a CuPc sample and similar effects may arise in other porphyrins and phthalocyanines.

(23) Y. Niwa, unpublished data.

(24) D. J. Hnatowich, J. Hudis, M. L. Perlman, and R. C. Ragani, *J. Appl. Phys.*, **42**, 4883 (1971).

(25) D. Betteridge, J. C. Carver, and D. M. Hercules, *J. Electron Spectrosc.*, **2**, 327 (1973).

Registry No. CoTPP, 14172-90-8; CuTPP, 14172-91-9; ZnTPP, 14074-80-7; H₂TBMAP, 7125-37-3; CuTBMAP, 26568-91-2; H₂-TBTAP, 7125-35-1; CuTBTAP, 52647-45-7; H₂Pc, 574-93-6; TiOPc,

26201-32-1; VOPc, 13930-88-6; MnPc, 14325-24-7; FePc, 132-16-1; CoPc, 3317-67-7; NiPc, 14055-02-8; CuPc, 147-14-8; ZnPc, 14320-04-8.

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Nuclear Magnetic Resonance Studies on the Structures of Some Substituted *N*-Alkylpyridinium Pentanitratolanthanate Ion Pairs in Solution

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A series of paramagnetic pentanitratolanthanate(III) complexes containing the *N*-octyl-4-phenylpyridinium and 2,4,6-trimethylbenzyl-4-methylpyridinium cations have been prepared and studied by proton nmr in low-dielectric solvents. The observed isotropic shift ratios are used to establish a time-average structure for the ion-pair complex. Comparison of the observed shift ratios with those derived from model calculations reveals that the pyridine ring is in rapid rotation with respect to the anion, and the lanthanide ion sits at an angle of roughly 90° with respect to the C₂ axis of the pyridine ring. An interionic distance of 7 Å is obtained from the measurements, indicating that the nmr technique detects predominantly contact ion pairs.

Introduction

In a recent article,¹ we have shown that when tetra-*n*-butylammonium cations are associated with paramagnetic pentanitratolanthanate(III) anions in ion-pair complexes in low-dielectric solvents, isotropic shifts arise in the nuclear magnetic resonance spectrum of the cation protons. These shifts were used to obtain information on the interionic distance, defined as the separation between the central nitrogen atom of the cation and the central lanthanide ion of the anion.

In general, the isotropic shift ($\Delta\nu_{\text{iso}}$) of a nmr signal from its normal position in a diamagnetic complex can be written as the sum of three terms:^{2,3} the Fermi contact term ($\Delta\nu_{\text{fc}}$) and the axial ($\Delta\nu_{\text{ax}}$) and rhombic ($\Delta\nu_{\text{rh}}$) dipolar terms (eq 1). It was shown¹ previously that the axial dipolar term is

$$\Delta\nu_{\text{iso}} = \Delta\nu_{\text{fc}} + \Delta\nu_{\text{ax}} + \Delta\nu_{\text{rh}} \quad (1)$$

by far the predominant effect in Ln(NO₃)₅²⁻ containing ion pairs. This term may be written

$$\Delta\nu_{\text{ax}} = f(\chi_1, \chi_2, \chi_3)(3 \cos^2 \alpha - 1)R^{-3} \quad (2)$$

where R is the distance between the lanthanide ion and the resonant proton, while α is the angle between R and the principal susceptibility axis χ_3 . The function $(3 \cos^2 \alpha - 1)R^{-3}$ is usually termed the geometric factor (GF). The function $f(\chi_1, \chi_2, \chi_3)$ cannot in general be evaluated for molecules in solution, since the principal susceptibilities χ_{1-3} are not known under these conditions. This term is usually eliminated by taking the isotropic shift of one proton on the cation as a reference ($\Delta\nu_j$)_{iso}, based on which ratios of the remaining cation proton shifts ($\Delta\nu_i/\Delta\nu_j$)_{iso} are computed. These observed shift ratios are solely functions of the geometry of the ion-pair complex.

$$(\Delta\nu_i/\Delta\nu_j)_{\text{iso}} = (3 \cos^2 \alpha_i - 1)R_i^{-3}/(3 \cos^2 \alpha_j - 1)R_j^{-3} \quad (3)$$

One may then, using known bond angles and distances in the cation, attempt to reproduce the observed shift ratios at suitable values of the interionic distance, by means of eq 3.

Obtaining geometrical information by this technique on tetraalkylammonium ions in ion pairs or on systems of similar flexibility is hindered by the difficulties inherent in calculating dipolar shift ratios from model structures in which the large number of different conformational possibilities for the alkyl chains must be taken into account. In other words, the structure of the cation in the ion-pair complex in solution is unknown, so that in general there are not enough nmr data available to establish both the cation structure and the structure of the ion-pair complex.

On the other hand, cations based on aromatic rings may be presumed to have structures in which the relative distance between the nuclei does not vary. Hence the cation structure is known in advance.

For this reason we have chosen to study dipolar shifts on cations of the *N*-alkyl- and *N*-benzylpyridinium class, at several concentrations and in several solvents. These are shown in Table I. Shift ratios have then been calculated from a variety of models for the ion-pair geometry, in which different degrees of mobility of the ions in the ion-pair complex have been assumed. These are then compared against the observed shift ratios in an attempt to establish the structure of the ion-pair complex on a time-average basis.

Experimental Section

Reagents. Rare earth oxides (99.9%, American Potash and Chemical Co.) were converted to the hydrated nitrates. 4-Phenylpyridine (Aldrich Chemical Co.) and γ -picoline (K & K Laboratories) were converted to the quaternary ammonium salts without further purification. All solvents used in this work were spectroscopic grade and were dried over molecular sieve for at least 24 hr before use.

Preparation of Complexes. 2,4,6-Trimethylbenzylpicolinium bromide, (TMBP)Br, prepared from γ -picoline and 2,4,6-trimethylbenzyl bromide,⁴ was allowed to react with stoichiometric amounts of hydrated rare earth nitrate and silver nitrate, in acetonitrile as previously described.¹ The resulting (TMBP)₂Ln(NO₃)₅ complexes are insoluble in dichloromethane and only slightly soluble in acetone at ordinary temperatures. They were recrystallized from hot acetonitrile-ethyl acetate mixtures.

N-Octyl-4-phenylpyridinium iodide, (oct-py-Ph)I, was prepared by refluxing stoichiometric amounts of 4-phenylpyridine and 1-iodooctane in acetonitrile for 72 hr. After removal of the solvent, the crystals were precipitated with benzene and stirred with triethyl ortho-

(1) I. M. Walker and D. H. Weeden, *Inorg. Chem.*, **12**, 772 (1973).

(2) G. N. La Mar, *J. Chem. Phys.*, **43**, 235 (1965).

(3) W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).

(4) L. Rosenthal and I. M. Walker, *Inorg. Chem.*, **11**, 2444 (1972).