were more intensified may implicate that such vibronic coupling occurs through the $C_\alpha C_\beta$ and $C_\alpha N$ bonds rather than the $C_\alpha C_m$ and $C_\beta C_\beta$ bonds, because the former contribute more to the modes around 1100–1300 cm^{-1}.[4] Alternatively negative interference of resonance effects of two different absorption bands[27] may have occurred to the methine bridge stretching modes upon excitation at 568.2 nm. For the determination of the alternatives, observation of detailed structure of excitation profile with dye laser is indispensable and such a study is under progress for Ni(OEC).

Acknowledgment. The authors wish to express their gratitude to Dr. Kenkichi Sonogashira, Osaka University, for the courtesy of measuring the mass spectra.

Registry No. Ni(OEC), 54676-28-7; Cu(OEC), 54676-27-6; Cu(OEC-d_2), 70101-72-3; Cu(OEC-$^{15}N_4$), 70116-74-4; Fe^{3+}(OEC)Cl, 54643-22-0; [Fe^{3+}(OEC)$(Im)_2$]Cl, 70096-17-2; Fe^{3+}(OEC)F, 54643-21-9.

References and Notes

(1) (a) Osaka University. (b) Kyoto University.
(2) (a) Kitagawa, T.; Ozaki, Y.; Kyogoku, Y. *Adv. Biophys.* **1978**, *11*, 153. (b) Spiro, T. G. *Biochim. Biophys. Acta* **1975**, *416*, 169 and references cited therein.
(3) Kitagawa, T.; Abe, M.; Ogoshi, H. *J. Chem. Phys.* **1978**, *69*, 4516.
(4) Abe, M.; Kitagawa, T.; Kyogoku, Y. *J. Chem. Phys.* **1978**, *69*, 4526.
(5) Gurinovich, G. P.; Sevchenko, A. N.; Solov'ev, K. N. "Spectroscopy of Chlorophyll and Related Compounds", Izdatel'stvo Nauka; Tekhnika: Minsk, 1968 (English translation; AEC-TR-7199).
(6) Lutz, M. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1972**, *275*, 497.
(7) Lutz, M.; Breton, J. *Biochem. Biophys. Res. Commun.* **1973**, *35*, 413.
(8) Lutz, M. *J. Raman Spectrosc.* **1974**, 2, 497.
(9) Lutz, M.; Kleo, J.; Reiss-Husson, F. *Biochem. Biophys. Res. Commun.* **1976**, *69*, 711.
(10) Nagata, Y.; Yamanaka, T.; Okunuki, K. *Biochim. Biophys. Acta* **1970**, *221*, 668.
(11) Ogoshi, H.; Watanabe, E.; Yoshida, Z.; Kincaid, J.; Nakamoto, K. *J. Am. Chem. Soc.* **1975**, *95*, 2845.
(12) Ogoshi, H.; Watanabe, E.; Yoshida, Z.; Kincaid, J.; Nakamoto, K. *Inorg. Chem.* **1975**, *14*, 1344.
(13) Bonnett, R.; Gale, I. A. D.; Stephenson, G. F. *J. Chem. Soc., Ser. C* **1967**, 1168.
(14) Hendra, P. J.; Loader, E. J. *Chem. Ind.* (*London*) **1968**, 718.
(15) Stoicheff, B. P. *Can. J. Phys.* **1957**, *35*, 730.
(16) Kitagawa, T.; Ogoshi, H.; Watanabe, E.; Yoshida, Z. *J. Phys. Chem.* **1975**, *79*, 2629.
(17) Kitagawa, T.; Abe, M.; Kyogoku, Y.; Ogoshi, H.; Watanabe, E.; Yoshida, Z. *J. Phys. Chem.* **1976**, *80*, 1181.
(18) McClain, W. M. *J. Chem. Phys.* **1971**, *55*, 2789.
(19) Miyazawa, T. *J. Mol. Spectrosc.* **1964**, *13*, 321.
(20) Lutz, M.; Kleo, J.; Gilet, R.; Henry M.; Plus, R.; Leicknam, J. P. *Proc. Int. Conf. Stable Isot. Chem., Biol., Med., 2nd* **1975**, 462.
(21) Spiro, T. G.; Strekas, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 338.
(22) Kitagawa, T.; Iizuka, T.; Saito, M.; Kyogoku, Y. *Chem. Lett.* **1975**, 849; *J. Am. Chem. Soc.* **1976**, *98*, 5169.
(23) Kitagawa, T.; Ogoshi, H.; Watanabe, E.; Yoshida, Z. *Chem. Phys. Lett.* **1975**, *30*, 451.
(24) Hirakawa, A.; Tsuboi, M. *Science* **1975**, *188*, 359.
(25) Tang, J.; Albrecht, A. C. In "Raman Spectroscopy"; Szymanski, H. A., Ed.; Plenum Press: New York, 1970; pp 33–68.
(26) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.
(27) Stein, P.; Miskowski, V.; Woodruff, W. H.; Griffin, J. P.; Werner, K. G.; Gaber, B. P.; Spiro, T. G. *J. Chem. Phys.* **1976**, *64*, 2159.

Contribution from the Chemistry Departments, Hunter College, City University of New York, New York, New York 10021, and Purdue University, West Lafayette, Indiana 47907

X-ray Photoelectron Spectra of *N*-Methyltetraphenylporphyrins: Evidence for a Correlation of Binding Energies with Metal–Nitrogen Bond Distances

DAVID K. LAVALLEE,*[1a] JOHN BRACE,[1b] and NICHOLAS WINOGRAD[1b,c]

Received August 3, 1978

X-ray photoelectron spectroscopic data are reported for *N*-methyltetraphenylporphyrin, its dicationic salt, and a number of metal complexes, with special attention given to the N 1s binding energies. The free-base N 1s energies are 397.6 and 399.9 eV, with the N–CH_3 nitrogen atom being perturbed to essentially the same extent as the N–H nitrogen atom. The spectrum of the acid shows an increase in the relative area of the peak at 399.9 eV, indicating protonation of the nonmethylated nitrogen atoms. The N 1s energies for the metal complexes (398.3 and 400.4 eV for Mn(*N*-CH_3TPP)Cl, 398.2 and 400.2 eV for Fe(*N*-CH_3TPP)Cl, 398.4 and 400.2 eV for Co(*N*-CH_3TPP)Cl, and 398.5 and 400.0 eV for Zn(*N*-CH_3TPP)Cl, with the lower energies due to the nonmethylated nitrogen atoms in each case) correspond to changes in the size of the metal atom. The metal atom perturbs the nonmethylated nitrogen atoms to a greater extent than the methylated nitrogen atom. The difference in these energies correlates in a linear fashion with differences in the respective metal–nitrogen bond lengths determined crystallographically. In the case of greatest difference in binding energies, Mn(*N*-CH_3TPP)Cl, the XPS data indicate a relatively strong interaction with the methylated nitrogen atom while in the case of the greatest bond length difference, Zn(*N*-CH_3TPP)Cl, very little interaction is evident.

Introduction

X-ray photoelectron spectroscopy (XPS or ESCA) has been applied to a limited extent in the study of molecules of biological interest.[2,3] Two features of XPS data indicate that this method may be useful in discerning differences in chemical bonding that would be advantageous in the study of such molecules: the range of binding energies for core electrons of one element in a variety of chemical environments is well removed from the range of energies for other biologically important elements, and the energy maxima for one element in a variety of chemical environments appear to correlate well with calculated electron densities.[4] The utility of the XPS technique must be judged in light of its sensitivity to changes in bond parameters.

A system providing for such an investigation is a series of metal complexes of *N*-methylporphyrins, especially of *N*-methyltetraphenylporphyrin.[5-15] These complexes serve as models of possible intermediates in the porphyrin metalation mechanism and have been used to investigate spectral[6,13] and kinetic properties[5,10,14-19] of porphyrins with significantly nonplanar coordination sites. They have been quite thoroughly characterized and provide a means for systematic comparison with non-N-alkylated porphyrins. The chlorozinc(II), chloromanganese(II), chlorocobalt(II), and chloroiron(II) com-

0020-1669/79/1318-1776$01.00/0 © 1979 American Chemical Society

plexes of *N*-methyltetraphenylporphyrin (*N*-CH_3TPP) have been characterized by X-ray crystallographic methods,[5,8,11,37] providing bond length and angle data for comparison with tetraphenylporphyrin (TPP) complexes.

One of the major differences between complexes of the N-methylated porphyrin and the nonmethylated porphyrin is the "hardness" of the *N*-CH_3TPP ligand relative to TPP. This characteristic has been demonstrated by a study of the infrared spectra of chloro-*N*-methyltetraphenylporphyrin complexes of Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II) in the metal-chloride stretching region (near 300 cm^{-1}).[7] In this region, the *N*-methylporphyrin complexes show the "normal" energies found for simple complexes such as $CoCl_4^{2-}$ while TPP complexes are "softer", showing lower stretching energies. Visible absorption spectra of solutions of *N*-CH_3TPP and *N*-methyldeuteroporphyrin IX dimethyl ester complexes[6,13] as well as infrared spectra in the "metal-sensitive" region[7] demonstrate a greater similarity of metal–ligand interactions among these complexes than among corresponding non-N-alkylated complexes.

In this report, we compare XPS data for free-base and protonated *N*-methyltetraphenylporphyrin with XPS data for other free-base porphyrins and data for several divalent metal complexes of *N*-CH_3TPP with results reported by Karweik and Winograd[3] for four-coordinate porphyrin and chlorin complexes of divalent metal ions. Attention is directed principally to N 1s binding energies since they are the most sensitive probe of bonding differences at the coordination sites of the porphyrins. The N 1s binding energies for the *N*-methyltetraphenylporphyrin free base, diacid cation, and metal complexes are compared with each other and with data for other porphyrins and metalloporphyrins in order to make assignments, to determine protonation sites, to explain basicity differences between *N*-methylated and nonmethylated porphyrins, and to discuss evidence for the structure of a postulated sitting-atop complex. The data for the *N*-methylmetalloporphyrins also indicate that binding energies depend upon metal–ligand bond lengths, an observation which has not previously been reported.

Experimental Section

The syntheses of *N*-methyltetraphenylporphyrin, Mn(*N*-CH_3TPP)Cl, Fe(*N*-CH_3TPP)Cl, Co(*N*-CH_3TPP)Cl, and Zn(*N*-CH_3TPP)Cl have been reported previously.[7] In all cases the complexes were purified by repeated crystallization and were identified by visible absorption and infrared spectroscopy.[7,13]

The XPS spectra were recorded on a Hewlett-Packard 5950A spectrometer utilizing monochromatized Al Kα X-ray radiation. The spectrometer system and the preparation of samples for use with this spectrometer have been described previously.[3] Charging of these insulating compounds was minimized by preparing sample films thin enough that gold photoelectrons from the substrate were observable. Although this afforded less than optimal sample counting rates, it was most important in obtaining consistent and reproducible peak shapes and binding energies. Quoted binding energies are referred to the gold $4f_{7/2}$ electron level at 83.8 eV and are reproducible to a precision of ±0.1 eV. No sample decomposition was evident, as the spectrometer analysis chamber remained near its base pressure of 2×10^{-9} torr (3×10^{-7} Pa) with all samples.

Results and Discussion

Earlier Work on Nitrogen-Containing Compounds. A number of papers in which X-ray photoelectron data for nitrogen-containing compounds are reported have appeared,[4,20-25] with the greatest range of compounds appearing in papers by Henrickson, Hollander, and Jolly[4] and by Nordberg et al.[20] For rather simple compounds, the results of CNDO calculations have been used to show an approximate correlation of N 1s binding energy with calculated charges on the nitrogen atom (approximately 10 eV per electron).[4] Thus, with a resolution of ±0.1 eV, a difference on the order of ±0.01 unit of charge should be evident from the XPS experiment.

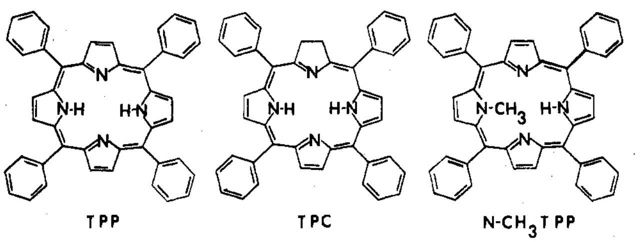

Figure 1. Structures of the free bases of *meso*-tetraphenylporphyrin, *meso*-tetraphenylchlorin, and *N*-methyl-*meso*-tetraphenylporphyrin (left to right). Metal complexes are formed by displacement of N–H hydrogen atoms. The "chlorin" nitrogen atom is the one in the ring with a saturated β–β pyrrole bond (the uppermost ring in the center structure).

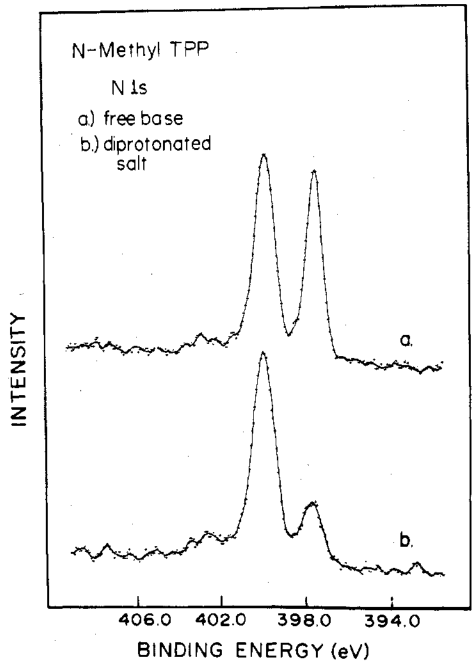

Figure 2. N 1s region of the X-ray photoelectron spectrum of (a) *N*-methyltetraphenylporphyrin and (b) the diprotonated perchlorate salt of *N*-methyltetraphenylporphyrin.

The range in N 1s binding energies for solids reported by Henrickson et al. is 396.6 eV (CrN) to 407.4 eV ($NaNO_3$), corresponding to a calculated range of nitrogen atom charges of −0.83 to +0.43 (CNDO method; the calculated range by extended Hückel methods is −1.40 to +2.52).

The effect of protonation of N 1s electron densities is demonstrated by the binding energies (BE) for piperidine (397.8 eV) and piperidine hydrochloride (400.4 eV)[20] which give $\Delta BE = 2.6$ eV and for the aromatic analogues, pyridine (398.0 eV) and pyridine hydrochloride (400.2 eV),[4] which give $\Delta BE = 2.2$ eV.[20]

***N*-Methyltetraphenylporphyrin.** N 1s XPS of *N*-methylporphyrin. N 1s XPS of *N*-methyltetraphenylporphyrin free base and the diacid cation can be used to deduce the hydrogen–nitrogen bonding pattern at the coordination site, including sites of protonation. The perturbations of the nitrogen core electrons caused by binding of a methyl group or a hydrogen atom are also evident from the XPS.

In the first reports of X-ray photoelectron spectroscopic studies of porphyrins,[3,22-25] it was determined that the porphyrin free bases such as tetraphenylporphyrin, shown in Figure 1, consist of two types of nitrogen atoms, with the higher binding energy assigned to the two nitrogen atoms that are bound to hydrogen atoms. The very short time scale of the XPS experiment does not preclude intramolecular hydrogen exchange which is rapid on the NMR time scale at

Table I. X-ray Photoelectron Spectroscopy Data (eV) for Some *N*-Methylporphyrin and Porphyrin Complexes

compd[a]	BE "sp^2" N 1s	BE "sp^3" N 1s	ΔBE	BE metal[b] $2p_{3/2}$	BE "porphyrin" N 1s	BE "chlorin" N 1s	ΔBE	BE metal $2p_{3/2}$	compd[c]
Mn(N-CH_3TPP)Cl	398.3	400.4	2.1	641.2 (3.4)					
Fe(N-CH_3TPP)Cl	398.2	400.2	2.0	709.3 (3.3)					
Co(N-CH_3TPP)Cl[d]	398.4	400.2	1.8	780.7 (2.7)	398.0	399.7	1.7	779.6	CoTPC
					398.3	399.0	0.7	854.9	NiTPC
					398.1	399.7	1.6	934.4	CuTPC
Zn(N-CH_3TPP)Cl	398.5	400.0	1.5	1022.2 (1.8)	397.6	398.5	0.9	1021.3	ZnTPC
H-N-CH_3TPP	397.6	399.9	2.3		397.4	399.3	1.9		H_2TPC

[a] Abbreviations: M(N-CH_3TPP)Cl, chloro(*N*-methyltetraphenylporphinato)metal(II) complex; MTPC, (tetraphenylchlorinato)metal(II) complex; ΔBE, difference in binding energy (all values in eV); fwhm, full width at half maximum. Binding energies are reproducible to ±0.1 eV. [b] Bandwidth (fwhm) in electron volts is given in parentheses. The greater bandwidth for paramagnetic ions is consistent with multiplet splitting observed previously for transition-metal ions: C. S. Fadley and D. A. Shirley, *Phys. Rev.*, **2**, 1109 (1970). [c] Reference 3. [d] Same values for N 1s (±0.1 eV) are also observed for Co(N-CH_3TPP)Br.

room temperature[27] but does rule out a symmetric structure in which the hydrogen atoms each bridge two nitrogen atoms.

In a similar manner, the N 1s portion of the XPS spectrum of *N*-methyltetraphenylporphyrin (Figure 2) shows peaks at 397.6 eV (based on Au $4f_{7/2}$ at 83.8 eV) and at 399.9 eV (assigned to the hydrogen- and methyl-bearing nitrogen atoms). The difference in binding energy of 2.3 eV is similar to differences for protonated and unprotonated nitrogen atoms in charged salts, as cited above, and for the two types of nitrogen in tetraphenylporphyrin (ΔBE = 2.0 eV).[3,22]

It is quite obvious from Figure 2 that the higher energy N 1s peak in the *N*-methyltetraphenylporphyrin spectrum is somewhat larger than the lower energy peak, the intensity ratio being 1.2.[28] For the parent unmethylated porphyrin, tetraphenylporphyrin, Niwa et al. also found that the higher energy peak was more intense (a ratio of 1.1); they attributed the difference to the presence of a satellite peak occurring at the same energy as the higher energy N 1s peak,[24] and such a satellite may also be present in our spectrum. The process giving rise to such satellite peaks is unclear at this time; a number of possible mechanisms exist but they are difficult to verify.[29,30]

The peak width of the 399.9 eV peak in the H-N-CH_3TPP N 1s spectrum is larger than that of the 397.6 eV peak (fwhm of 1.09 and 0.92 eV, respectively), as one might expect from the fact that the higher energy peak arises from two different types of nitrogen atom (N-CH_3 and N-H) which have very similar binding energies. The peak widths for the two pairs of nitrogen atoms in tetraphenylporphyrin are both about 0.95 eV.[24] Assignment of the N 1s peaks in H-N-CH_3TPP is verified by the increase in relative intensity of the higher energy peak with protonation (Figure 2). The 397.6-eV peak does not totally disappear even though absorption spectra of the compound indicate complete formation of H_3-N-$CH_3$$TPP^{2+}$ in solution;[15] apparently some acid is lost under the conditions of the XPS experiment.

The different peak positions for the nitrogen atoms with and without protons demonstrate that in *N*-methyltetraphenylporphyrin, as in tetraphenylporphyrin, the hydrogen atom is localized on one nitrogen atom and does not bridge two or more nitrogen atoms. The spectrum also demonstrates, as expected, that the methyl-bearing nitrogen atom is less basic than the others since an additional peak at about 402 eV would be expected to result from protonation of the methyl-bearing nitrogen whereas formation of H_3-N-$CH_3$$TPP^{2+}$ only causes an increase in intensity of the 400-eV peak.

By using a porphyrin with different substituents on the pyrrole rings, one might attempt to define the probability of the hydrogen atom position by using XPS. The nearly identical N 1s energies found by Karweik and Winograd for octaethylporphyrin (each β pyrrole position occupied by an ethyl group) and *meso*-tetraphenylporphyrin (399.2 and 397.2 vs. 399.0 and 397.0 eV, respectively)[3], however, argue against the feasibility of this experiment.

As H-N-CH_3TPP is protonated, there is no discernible shift in energy of the N 1s peaks but only an increase in relative intensity of the peak assigned to N–H and N–CH_3 nitrogen in the free base. Likewise, Zeller and Hayes[22] found only an increase in the higher energy peak (399.2 eV) of H_2TPP when it is protonated to form H_4TPP^{2+}. These results indicate that the difference in the equilibrium constant for addition of the second and first protons to the neutral free base (generally about a factor of 10–100)[31] should be accounted for by features of the monoprotonated cation other than the charge on the remaining uncoordinated nitrogen atom. One might be tempted to infer that the greater basicity of H-N-CH_3TPP relative to H_2TPP (pK_a's of 5.6 and 4.4, respectively)[15] was, at least in part, due to the greater electron density on the nitrogen atom coordination sites. The XPS core energies for these nitrogen atoms (397.6 eV for H-N-CH_3TPP vs. 397.0[3] or 397.1[22] eV for H_2TPP) indicate exactly the opposite,[32] supporting the contention that the major reason for the increased basicity of *N*-methyporphyrins is steric deformation.[33] It would be interesting to obtain X-ray photoelectron spectra of *N*-methyletioporphyrin and *N*-methylcoproporphyrin which have pK_a's of 14 and 13 for the formation of the monocation, respectively, since they may exhibit a contribution from electron density at the nitrogen that is not found for H-N-CH_3TPP.[34,35]

Metalloporphyrin Complexes. The XPS data for metal complexes of non-N-methylated porphyrins and chlorins, including a complex proposed to have a sitting-atop structure, have several features in common with data for N-CH_3TPP complexes. Karweik and Winograd have tabulated XPS metal $2p_{3/2}$ or $3d_{5/2}$, N 1s, and C 1s binding energies for a number of four-coordinate porphyrin and chlorin complexes (Mg(II), Zn(II), Ni(II), Co(II), Cu(II), and Ag(II) complexes of tetraphenylporphyrin and tetraphenylchlorin; see Table I).[3] The C 1s binding energies of these complexes varied from 283.8 to 284.3 eV with reproducibilities of ±0.1 eV and were not discussed in detail. (Note that we have corrected all binding energies from ref 3 by −0.2 eV to account for the difference in reference-level energy.) The most notable features of their data involved N 1s binding energies. The metallochlorin complexes have spectra that can be deconvoluted into two peaks with an approximately 3:1 area ratio. The higher energy peak is the less intense and is assigned to the reduced pyrrole ring (the "chlorin" nitrogen). The binding-energy difference between the peaks was 0.8 ± 0.1 eV for the diamagnetic complexes (Mg(II), Zn(II), and Ni(II)) and 1.6–1.9 for the paramagnetic complexes (Co(II), Cu(II), and Ag(II)). In each case the more intense peak was

Table II. Some Structural Features of Chloro-*N*-methyltetraphenylporphyrin Complexes

metal ion	ionic radius,[a] Å G	P	L	electroneg[b]	M-N bond lengths,[c] Å	av, Å	$M-NCH_3$ bond length	diff,[d] Å	ΔBE, eV
Mn(II)	0.91	0.80	0.93	1.55	2.156, 2.156, 2.118	2.143	2.368	0.225	2.1
Fe(II)	0.83	0.76	0.90	1.83	2.118, 2.116, 2.082	2.105	2.329	0.224	2.0
Co(II)	0.82	0.74	0.88	1.88	2.063, 2.063, 2.016	2.047	2.381	0.334	1.8
Zn(II)	0.69	0.74		1.65	2.081, 2.089, 2.018	2.063	2.530	0.467	1.5

[a] G = Goldschmidt, P = Pauling, L = Ladd: F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley, New York, 1972, p 52. [b] J. W. Buchler, C. Puppe, K. Rohbock, and H. R. Schneehage, *Ann. N. Y. Acad. Sci.*, 206, 117 (1973). [c] References 5, 9, 11, and 37. [d] The difference between the average M-N bond length and the $M-NCH_3$ bond length.

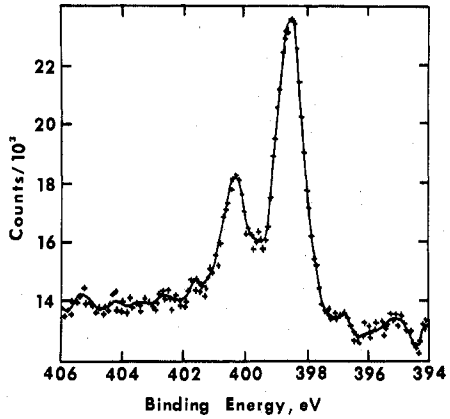

Figure 3. N 1s region of the X-ray photoelectron spectrum of chloro(*N*-methyltetraphenylporphinato)cobalt(II), showing the peak of the methylated nitrogen at higher energy than that due to the three nonmethylated nitrogens.

within ±0.1 eV of the single peak found for the corresponding metalloporphyrin complex, and the range was 397.6 eV (Mg(II) and Zn(II)) to 398.3 eV (Ni(II) and Ag(II)).

The XPS data for chloro-*N*-methyetetraphenylporphinato complexes of Mn(II), Fe(II), Co(II), and Zn(II) are presented in Table I along with Karweik and Winograd's data for some tetraphenylchlorin complexes. A typical X-ray photoelectron spectrum of one of these complexes is presented as Figure 3. It is evident from these data that the binding energies of the three "sp^2" nitrogen atoms of the *N*-methylporphyrin complexes are in the range of the "porphyrin" N 1s energies while the methylated nitrogen ("sp^3") is very similar in energy to the "chlorin"-type nitrogens. The general trend in both sets of data is for the complexation of the metal ion to raise the binding energy of the 1s electrons of the "sp^2" or "porphyrin" nitrogens.

Theophanides and co-workers have discussed the XPS of a platinum complex of hematoporphyrin which is proposed to have a sitting-atop structure with the platinum atom bound to two of the porphyrin nitrogen atoms and hydrogen atoms bound to the remaining two.[36] The N 1s binding energies are 398.6 and 399.9 eV, respectively. These values are quite close to those we find for Zn(*N*-CH_3TPP)Cl, which are 398.5 eV for the nitrogen atoms bound to zinc and 400.0 eV for the methylated nitrogen atom (which shows little indication of perturbation by the zinc—the value for the nitrogen atom on the free base is 399.9 ± 0.1 eV). Our results support the structure Theophanides has proposed for the *cis*-$PtCl_2H_2$ (hematoporphyrin IX) complex since: (1) the N 1s binding energy for a nitrogen atom bound to a hydrogen atom in a porphyrin with a very nonplanar structure, namely, H-*N*-CH_3TPP, is at essentially the same energy as the N 1s for those nitrogens in the platinum complex that are proposed to be bound to hydrogen but not platinum, (2) the N 1s energy for the platinum-bound nitrogen atoms is reasonable when compared with our data for complexes that are severely ruffled—a structural feature Theophanides proposes for his platinum complex, and (3) bonding of the metal atom to the "sp^3" nitrogen atoms of a porphyrin complex should result in N 1s energies significantly greater than the 399.9 eV found in Theophanides' complex.

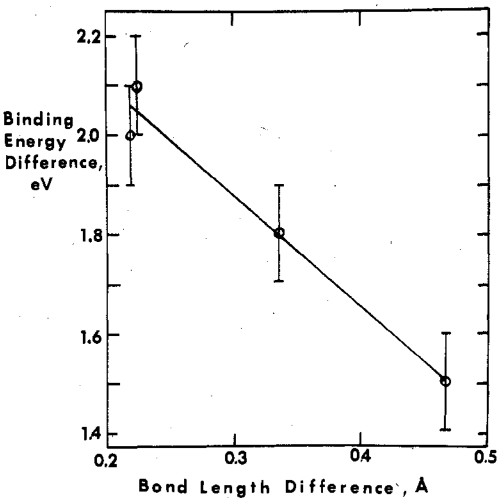

Figure 4. Correlation of the difference between the N 1s binding energies of the methylated and nonmethylated nitrogen atoms of Mn(*N*-CH_3TPP)Cl, Fe(*N*-CH_3TPP)Cl, Co(*N*-CH_3TPP)Cl, and Zn(*N*-CH_3TPP)Cl and the difference in the metal–nitrogen bonding lengths (the metal to methylated nitrogen bond length minus the average metal to nonmethylated nitrogen bond lengths).

The series of *N*-CH_3TPP complexes discussed herein also offers an unusual opportunity for observing the effect of metal–ligand bond length changes on binding energies. The metal–methylated nitrogen bond lengths show a relatively large variation while the other metal–nitrogen bond lengths remain essentially normal. From the data presented in Table II, there appears to be a correlation between the difference in metal–methylated nitrogen and metal–nonmethylated nitrogen bond lengths and the order of ionic radii of metal ions. Thus the smallest ion, Zn(II), shows the largest difference in bond lengths while the largest ion, Mn(II), shows the least difference. From the X-ray diffraction studies of the crystal and molecular structures of the complexes Mn(*N*-CH_3TPP)Cl,[9] Fe(*N*-CH_3TPP)Cl,[37] Co(N-CH_3TPP)Cl,[8,11] and Zn(*N*-CH_3TPP)Cl,[5] it is evident that the bond lengths from Mn(II), Fe(II), and Co(II) to the methylated nitrogen can be considered to indicate some bonding whereas the long Zn(II)–N–CH_3 bond appears to be too long for significant bonding interactions. It was hoped that the XPS of these complexes would shed light on the degree of interaction in these cases.

From the data presented in Table I, two general trends appear in the binding energies of the *N*-methyltetraphenylporphyrin complexes: as ionic size decreases, there is a trend toward increasing binding energy for the nonmethylated (sp^2) nitrogen atoms and decreasing binding energy for the methylated (sp^3) nitrogen atom. For the purpose of comparing one *N*-methylporphyrin complex with another, differences in the energies of these two types of nitrogen atoms are perhaps more reliable than absolute values. For example, Zeller and

Hayes reported values of N 1s binding energies of 399.1 and 397.2 eV for H_2TPP[22], Karweik and Winograd reported values of 399.0 and 397.0 eV,[3] and the values reported by Niwa et al. are 400.2 and 398.2 eV[24]—much higher in absolute energy, but with a consistent difference in binding energies of 2.0 eV.

As shown in Table II and Figure 4 there is a consistent trend of the difference in binding energies of the two types of nitrogen atom with the differences in the metal–nitrogen bond lengths between the two types of nitrogen atoms (and also with ionic radii for the metal atoms) but no apparent correlation with metal-atom electronegativities. A greater degree of bonding to the methylated nitrogen atom, indicated by a higher N 1s binding energy, is shown for the larger metal ion, in the order Mn(II) > Fe(II) > Co(II) > Zn(II). The dominant feature in the binding of the metal atom to the methylated nitrogen atom is the constraint imposed by the bonding of the other three nitrogen atoms. The shorter those bonds are, the longer and weaker is the bond to the methylated nitrogen atom. In going from the free base to the manganese(II) complex, the N 1s levels are similarly perturbed (0.5 eV for the $N–CH_3$ nitrogen and 0.7 eV for the other three nitrogens) while for the zinc(II) complex the interaction of the metal with the methylated nitrogen atom is much smaller than its interaction with the other three nitrogen atoms (0.1- vs. 0.9-eV perturbations).

Summary

X-ray photoelectron spectroscopy provides very clear results when large differences in bonding are in question, as, for example, in showing that the nitrogen-bound hydrogen atom in free-base *N*-methyltetraphenylporphyrin is bound to one nitrogen atom rather than being bound to more than one nitrogen atom and in showing that only the nonmethylated nitrogen atoms are protonated when the diacid salt is formed. Even subtleties in bonding can be probed by this technique, as shown by the trend in N 1s binding energies and metal–nitrogen interactions deduced from small changes in bond lengths. It should be borne in mind, however, that the reproducibility in binding energies by current techniques is rather large (~0.1 eV) and is comparable with differences found in the latter correlation.

Acknowledgment. We appreciate the technical assistance of Marie-Claude Hayoit de Termicourt. We express gratitude to the donors of the Petroleum Research fund, administered by the American Chemical Society, for partial support of this research and to the NSF for Grant MPS75-9308 and the AFOSR for Grant AF762974.

Registry No. Mn(N-CH_3TPP)Cl, 59765-80-9; Fe(N-CH_3TPP)Cl, 64813-94-1; Co(N-CH_3TPP)Cl, 51552-52-4; Zn(N-CH_3TPP)Cl, 59765-81-0; Co(N-CH_3TPP)Br, 64813-97-4; H-N-CH_3TPP, 51552-53-5.

References and Notes

(1) (a) Hunter College, C.U.N.Y. (b) Purdue University. (c) Guggenheim Fellow, 1977–1978.

(2) J. A. Wurzbach, D. J. Grunthaner, D. M. Dooley, H. B. Gray, F. J. Grunthaner, R. R. Gay, and E. I. Solomon, *J. Am. Chem. Soc.*, **99**, 1257 (1977), and references therein.

(3) D. H. Karweik and N. Winograd, *Inorg. Chem.*, **15**, 2336 (1976), and references therein.

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

(5) D. K. Lavallee, A. Kopelove, and O. P. Anderson, *J. Am. Chem. Soc.*, **100**, 3025 (1978).

(6) D. K. Lavallee and M. J. Bain-Ackerman, *Bioinorg. Chem.*, **8**, 311 (1978).

(7) D. K. Lavallee, *Inorg. Chem.*, **17**, 231 (1978).

(8) O. P. Anderson and D. K. Lavallee, *Inorg. Chem.*, **16**, 1634 (1977).

(9) O. P. Anderson and D. K. Lavallee, *J. Am. Chem. Soc.*, **99**, 1404 (1977).

(10) D. K. Lavallee, *Inorg. Chem.*, **16**, 955 (1977).

(11) O. P. Anderson and D. K. Lavallee, *J. Am. Chem. Soc.*, **98**, 4670 (1976).

(12) D. K. Lavallee and M. J. Bain, *Inorg. Chem.*, **15**, 2090 (1976).

(13) D. K. Lavallee, *Bioinorg. Chem.*, **6**, 219 (1976).

(14) D. K. Lavallee, *Inorg. Chem.*, **15**, 691 (1976).

(15) D. K. Lavallee and A. E. Gebala, *Inorg. Chem.*, **13**, 2004 (1974).

(16) C. Stinson and P. Hambright, *J. Am. Chem. Soc.*, **99**, 2357 (1977).

(17) C. Stinson and P. Hambright, *Inorg. Chem.*, **15**, 3181 (1976).

(18) B. Shah, B. Shears, and P. Hambright, *J. Am. Chem. Soc.*, **93**, 776 (1971).

(19) B. Shah, B. Shears, and P. Hambright, *Inorg. Chem.*, **10**, 1828 (1971).

(20) R. Nordberg, R. G. Albridge, T. Bergmach, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1967).

(21) J. J. Jack and D. M. Hercules, *Anal. Chem.*, **43**, 729 (1971).

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

(23) D. H. Karweik, N. Winograd, D. G. Davis, and K. M. Kadish, *J. Am. Chem. Soc.*, **96**, 591 (1974).

(24) Y. Niwa, M. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974); *Inorg. Chem.*, **13**, 2891 (1974).

(25) M. Falk, O. Hofer, and H. Lehner, *Monatsh. Chem.*, **105**, 366 (1974).

(26) Caution must be exercised in abstracting binding energies from the literature. Counterions can cause differences of several tenths of an electron volt in N 1s binding energies as evidenced in the data in ref 21. Values cited for N 1s binding energies for the same compounds differ by up to 0.4 eV in comparing data in ref 4, 20, and 21.

(27) C. B. Storm, Y. Teklu, and E. Sokoloski, *Ann. N. Y. Acad. Sci.*, **206**, 631 (1973).

(28) We suspected that the free base may have been partially protonated, leading to a more intense high-energy peak. Treatment of the porphyrin with 0.5 M NaOH, however, did not reduce the ratio below 1.2.

(29) C. K. Jorgensen, *Struct. Bonding (Berlin)*, **24**, 1 (1975).

(30) W. L. Jolly, *Top. Curr. Chem.*, **71**, 150 (1977).

(31) P. Hambright in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, New York, 1975, p 238.

(32) For a discussion of the possible complications arising from electronic relaxation effects in correlating core binding energies to electron density and support for such a correlation in the case of porphyrins, see ref 3.

(33) A. H. Jackson and G. R. Dearden, *Ann. N. Y. Acad. Sci.*, **206**, 151 (1973).

(34) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

(35) A. Neuberger and J. J. Scott, *Proc. R. Soc. London, Ser. A*, **213**, 307 (1952).

(36) J. P. Macquet, M. M. Millard, and T. Theophanides, *J. Am. Chem. Soc.*, **100**, 4741 (1978).

(37) D. K. Lavallee, A. Kopelove, and O. P. Anderson, submitted for publication.