Hydrogen Bonding. In the parent amine dihydrohalides, a complex series of absorptions is found at 2600–2800 (very strong) and 2400–2600 cm^{-1} (strong), which became attenuated on deuteration, indicating that the N–H motion is involved.[21] The positions of these bands are in agreement with the piperidinium and morpholinium salts[1] and other secondary amine hydrohalides.[21,22] Furthermore a medium-intensity band appears at 3200–3250 cm^{-1}.

The bending N–H mode at 1612, 1540 and 1618, 1568, 1532 cm^{-1} in dihydrochloride and dihydrobromide salts, respectively, which disappears on deuteration, is not sensitive to the CuX$_4^{2-}$ geometry contrary to that found with piperidinium and morpholinium cations.[1] Instead, the bending N–H modes appearing at 914–930 and at 560–570 cm^{-1} in the dihydrohalide salts, which disappear on deuteration, are shifted to higher energies (990 and 570 cm^{-1}, respectively) in the complexes which approach square-planar configuration and remain stationary or are slightly lowered in energy (910 and 550 cm^{-1}, respectively) in the complexes with a distorted tetrahedral symmetry, in accordance with a stronger hydrogen bond in the former.

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Registry No. (pipzH$_2$)CuCl$_4$, 59830-85-2; (pipzH$_2$)$_2$CuCl$_6$, 59830-86-3; (pipzH$_2$)CuCl$_3$Br, 59872-30-9; (pipzH$_2$)CuCl$_2$Br$_2$, 59872-32-1; (pipzH$_2$)$_2$CuCl$_5$Br, 59830-87-4; (pipzH$_2$)CuBr$_4$, 59830-88-5; (pipzH$_2$)$_2$CuCl$_2$Br$_4$, 59830-89-6; (pipzH$_2$)$_2$CuBr$_6$, 59830-90-9; (pipzH$_2$)Cu$_2$Cl$_6$, 59872-33-2; (pipz)(HCl)$_2$, 142-64-3; (pipz)(HBr)$_2$, 59813-05-7; (pipz)(HCl)(HBr), 59813-06-8; pipzHBr, 59813-07-9; pipzHCl, 6094-40-2.

References and Notes

(1) G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *J. Coord. Chem.*, in press.

(2) D. N. Anderson and R. D. Willett, *Inorg. Chim. Acta*, **5**, 41 (1971).

(3) G. B. Birrell and B. Zaslow, *J. Inorg. Nucl. Chem.*, **34**, 1751 (1972).

(4) D. W. Smith, *J. Chem. Soc. A*, 2529 (1969).

(5) D. W. Smith, *J. Chem. Soc. A*, 2900 (1970).

(6) J. Demuynck, A. Veillard, and U. Wahlegren, *J. Am. Chem. Soc.*, **95**, 5563 (1973).

(7) R. L. Harlow, W. J. Wells, III, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **14**, 1768 (1975), and references cited therein.

(8) R. D. Willett, *J. Chem. Phys.*, **44**, 39 (1966).

(9) R. D. Willett and O. L. Liles, Jr., *Inorg. Chem.*, **6**, 1666 (1967).

(10) G. Felsenfeld, *Proc. R. Soc. London, Ser. A*, **236**, 506 (1956).

(11) (a) R. D. Willett, J. R. Ferraro, and M. Choca, *Inorg. Chem.*, **13**, 2919 (1974), and references cited therein; (b) R. D. Willett, J. A. Haugen, J. Lebsack, and J. Morrey, ibid., **13**, 2510 (1974), and references cited therein.

(12) D. N. Anderson and R. D. Willett, *Inorg. Chim. Acta*, **8**, 167 (1974).

(13) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 1252 (1969).

(14) W. J. Geary, *Coord. Chem. Rev.*, **7**, 110 (1971).

(15) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960, p 406.

(16) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

(17) J. T. Dunsmuir and A. P. Lane, *J. Chem. Soc. A*, 404 (1971).

(18) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

(19) R. J. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(20) D. M. Adams and P. J. Lock, *J. Chem., Soc. A*, 620 (1967).

(21) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, N.Y., 1959, p 259.

(22) N. B. Colthrum, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, N.Y., 1964, p 282.

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Nitrogen Charge Distributions in Free-Base Porphyrins, Metalloporphyrins, and Their Reduced Analogues Observed by X-Ray Photoelectron Spectroscopy[1a]

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The metal, N 1s, and C 1s XPS binding energies for the free-base compounds (H$_2$OEP, H$_2$TPrP, H$_2$TPP, H$_2$TPC, H$_2$TPBC), the metalloporphyrins (MgTPP, ZnTPP, CoTPP, CuTPP, NiTPP, AgTPP), and the metallochlorins (MgTPC, ZnTPC, CoTPC, CuTPC, NiTPC, AgTPC) are reported. The N 1s binding energies plus additional information from theoretical calculations and NMR, uv–vis, and ir spectroscopy show that reduction of the free bases slightly decreases the electron density of the nitrogen and only subtly changes their XPS spectra. The replacement of the free-base protons by a metal ion to form the metalloporphyrin increases the symmetry of the molecule and also introduces an electron-withdrawing group into the center of the ligand which increases the N 1s binding energy as the metal ion electronegativity increases. Finally these results are used to show that both effects are found in metallochlorins. In both metalloporphyrins and metallochlorins differences in the spectral features of paramagnetic and diamagnetic ions are noted.

Introduction

The comparison of data derived from several spectroscopic methods has been a standard modus operandi for establishing the structure and bonding in metal chelates. To this end nearly every available technique has been applied to porphyrins and their derivatives. Most of the early studies were primarily concerned with defining the effect of the porphyrin structure and substituents on the ultraviolet–visible absorption[2–8] and emission[9,10] spectral patterns. However, ESR,[11–14] ir,[15–18] x-ray crystallographic,[19–21] ^{1}H,[22] ^{13}C,[23] and ^{15}N,[24] NMR, Raman,[25,26] and electrochemical[27–30] techniques have all been used to study the porphyrin macrocycle. In most cases these studies were combined with molecular orbital calculations to support the measurements. The results of these experiments and calculations have shown the porphyrin ring is a planar, aromatic macrocycle which behaves as a quadridentate, soft-base ligand.[31]

In Figure 1, some of the variations available with the porphyrin ligand are illustrated. As indicated in Figure 1a, the β carbons (C$_\beta$)[32] may incorporate ethyl substituents to form the molecule of 1,2,3,4,5,6,7,8-octaethylporphyrin free base. Alternately as shown in Figure 1b the central porphine skeleton may be substituted on the meso carbon positions (C$_m$) to form $\alpha,\beta,\gamma,\delta$-*meso*-tetraphenylporphyrin. Finally, as shown in Figure 1c and d, the ring may be reduced to the corresponding chlorin or bacteriochlorin. Formally, the reduction occurs on the β carbons on ring IV to form the chlorin and on rings II and IV to form the bacteriochlorin. Although

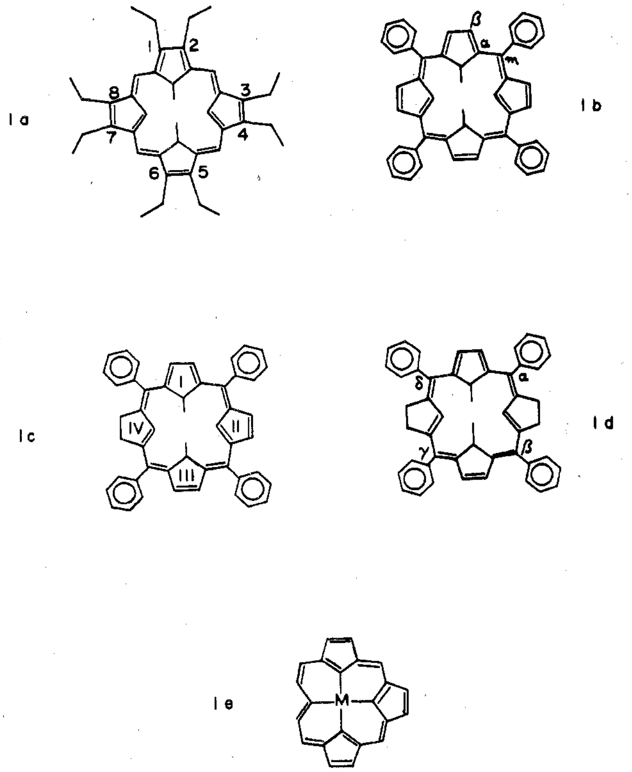

Figure 1. Structures of porphyrins studied: (a) H_2OEP with numbering of β carbon atoms; (b) H_2TPP with carbon position lettering; (c) H_2TPC with pyrrole ring numbering; (d) H_2TPBC with meso carbon lettering; (e) metallochlorin model used by Gouterman.

further modifications are possible and commonly found, only these will be considered in this paper. Because the ligand is very polarizable, it has special facility in stabilizing higher oxidation state metal ions such as $V^{IV}O(TPP)$, $Ag^{III}OEP^+ClO_4^-$, and $(Fe^{IV}TPP)O$ by electron donation through the metal–nitrogen σ bonds.[33,34] Chlorins have been shown in the broadest sense to be similar in their properties to the unreduced porphyrins.[4,5,22,35] However, a moderately complete description of the properties of these molecules is hampered by the paucity of the studies including these ligands in more than a superficial manner.

In the last 2 years x-ray photoelectron spectroscopy (XPS or ESCA) has been applied to the study of porphyrins and chlorins. The earliest reports included the description of the differences between metalloporphyrins and the porphyrin free bases, the congruence of the information gained from molecular orbital calculations and XPS studies, and the identification of the unusual oxidation states in metalloporphyrins. XPS was able to determine the presence of two distinctly different, nonequivalent nitrogen types in the porphyrin free base,[36-39] which can be contrasted with the single, equivalent nitrogen peak found in metalloporphyrins.[37,38] The presence of the two nitrogen peaks in the free-base spectrum is due to the protonation of two of the four pyrrole nitrogens formally found on rings I and III.[22] These measurements eliminated the possibility of a bridged free-base structure as had been postulated earlier which would require a single, equivalent nitrogen peak. A later study was directed to establish the identity of the oxidation product of silver(II) octaethylporphyrin, $(Ag^{II}OEP)$.[37] Through the interpretation of the metal and nitrogen binding energy shifts, the oxidation product was assigned to be $Ag^{III}OEP^+ClO_4^-$. Efforts have also been aimed at correlating the XPS results with charge densities calculated via MO theory. Quantitative correlations have so far been illusive,[39] although certain qualitative features of the calculations are mirrored in the N 1s binding energy shifts.

Table I. Free-Base Binding Energies (eV)

Compd	>N-H (N1, N3)	≡N (N2, N4)	ΔBE	Carbon
H_2OEP	399.4 (±0.05)	397.4 (±0.05)	2.0	284.6 (±0.1)
H_2TPrP	399.3 (±0.1)	397.3 (±0.1)	2.0	284.1 (±0.1)
H_2TPP	399.2 (±0.05)	397.2 (±0.05)	2.0	284.0 (±0.1)
H_2TPC	399.5 (±0.05)	397.6 (±0.05)	1.9	284.1 (±0.1)
H_2TPBC	399.6 (±0.05)	397.8 (±0.05)	1.8	284.6 (±0.1)

From the previous studies and the report to follow it is apparent that the N 1s binding energies are the most sensitive probe for describing the charge distribution in porphyrins. This is true for three reasons. First, the nitrogens are bound to both the central metal and the carbon ring skeleton. Therefore, the four nitrogens are the nexus of the σ metal–nitrogen bonding orbitals and the carbon–nitrogen π-bonding orbitals. Second, there are only four nitrogens while there are up to 44 carbons to dilute single-electron effects. Third, in many cases, there is no change in the metal ion binding energy with small changes in the charge distribution between the macrocycle and the metal orbitals, making them relatively insensitive to structural alterations.

It is the intention of this work to show that reducing the β carbons of rings II and IV to form the free-base chlorin and bacteriochlorin decreases the electron density on the nitrogens which is visible through the increase in the N 1s binding energies upon reduction and that increasing the metal ion electronegativity reduces the nitrogen electron population in metalloporphyrins causing the N 1s binding energy to increase. These two results will be combined to describe the nitrogen binding energy pattern produced by the metallochlorins. In both the metalloporphyrins and metallochlorins special attention will be given to differences in the binding of diamagnetic and paramagnetic metal ions to the macrocyclic ligand as evidenced by differences in the N 1s peak shapes and binding energies.

Experimental Section

The ZnTPP, ZnTPC, MgTPP, MgTPC, NiTPP, NiTPC, CoTPP, CoTPC, CuTPP, CuTPC, AgTPP, AgTPC, H_2TPP, and H_2TPC were donated by Dr. Alan Adler of the New England Institute. H_2TPBC was supplied by Professor G. S. Wilson of the University of Arizona. The compounds had optical spectra matching literature values[4] and were used without further purification.

The XPS spectra are measured on a Hewlett-Packard 5950A spectrometer using monochromatized Al Kα x-ray radiation. The spectrometer system has been previously described.[40,41] The samples are prepared by spreading ~10 μg of the porphyrin or chlorin on a gold-clad copper blank and then burnishing the sample with a sapphire bead mounted on an aluminum handle. When the sample appears like a thin lacquer film on the blank, the blank is mounted on the probe for insertion into the spectrometer. Burnished samples show no sign of charging since the measured binding energies from one sample to another are highly reproducible and since the peaks do not shift when the sample is flooded with low kinetic energy electrons. Samples prepared by evaporating ether, acetone, or benzene solutions of the porphyrins onto the gold blanks are unacceptable unless the evaporated material is also burnished. Samples intimately mixed with graphite also yield erratic binding energies. All binding energies are referenced to the gold $4f_{7/2}$ electron level at 84.0 eV and are reproducible to a precision of ≤±0.1 eV.

The spectra of the metallochlorins are deconvoluted using the Du Pont 210 curve resolver. Peak full-width half-maxima are obtained from the corresponding porphyrin peaks. The same fwhm are used for both peaks in the chlorin spectra. Gaussian and skewed Gaussian peak shapes are used to deconvolute the chlorin spectra (vide infra).

Results

The compounds studied in this paper will be divided into three classes, each with a characteristic N 1s spectrum as illustrated in Figure 2. The first class of compounds consists of the free bases which include H_2OEP, H_2TPrP, H_2TPP,

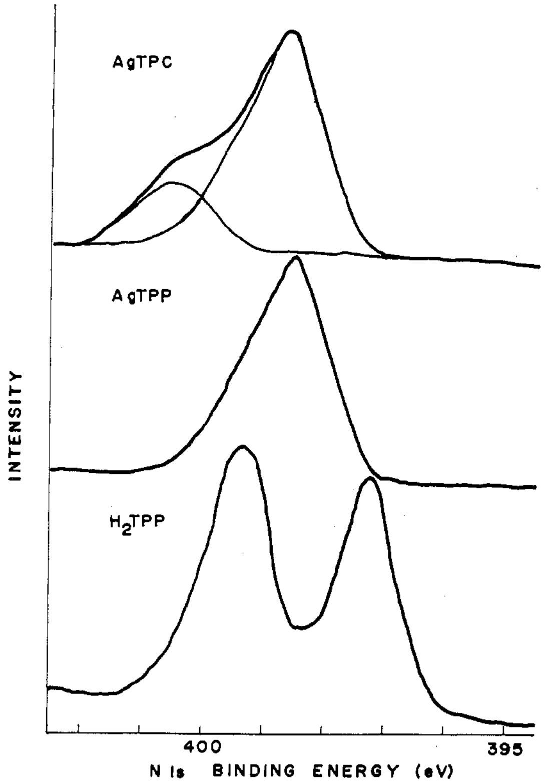

Figure 2. N 1s peak shapes for three typical porphyrins and chlorins.

Table II. Metalloporphyrin and Metallochlorin Binding Energies (eV)[a]

Compd	"Porphyrin" nitrogen 1s	"Chlorin" nitrogen 1s	Metal	Metal level	Carbon 1s
MgTPP	397.8				284.0
MgTPC	397.8	398.7			284.3
ZnTPP	397.8		1021.5	$2p_{3/2}$	284.0
ZnTPC	397.8	398.7	1021.5	$2p_{3/2}$	284.1
NiTPP	398.5		855.1	$2p_{3/2}$	284.5
NiTPC	398.5	399.2	855.1	$2p_{3/2}$	284.5
CoTPP	398.1		779.8	$2p_{3/2}$	284.1
CoTPC	398.2	399.9	779.8	$2p_{3/2}$	284.3
CuTPP	398.2		934.6	$2p_{3/2}$	284.2
CuTPC	398.3	399.9	934.6	$2p_{3/2}$	284.4
AgTPP	398.5		367.6	$3d_{5/2}$	284.3
AgTPC	398.6	400.5	367.6	$3d_{5/2}$	284.1

[a] Binding energies are reproducible to ±0.1 eV.

H_2TPC, and H_2TPBC. The binding energies for these compounds and the spacings between the nitrogen peaks are listed in Table I. Although the C 1s binding energies are also listed here (and in Table II) for reference, they will not be discussed for the reasons given previously and because XPS cannot resolve the composite carbon peak[38] into separate peaks for each type of chemically equivalent carbon found in the ligands studied. Note, however, that the C 1s peak position does vary by about 0.5 eV making it somewhat unsuitable as an internal reference peak. As can be seen in both Figure 2 and Table I, this class of compound is characterized by the presence of two nitrogen peaks having an area ratio of 1.17 (±0.04):1 for the protonated and unprotonated nitrogens. This deviation from the expected intensity ratio of 1:1 has been observed for other porphyrin and azaporphyrin derivatives.[38] It is apparently due to a weak satellite peak associated with the N 1s peak of lower binding energy overlapping with the N 1s peak of higher binding energy. For the three unreduced porphyrins the peak separation is 2.0 eV and is lowered by 0.1 eV for each pyrrole ring reduced while proceeding structurally from the porphyrin to the bacteriochlorin. This smaller splitting is statistically significant since the free-base N 1s binding energies are reproducible to 0.05 eV and since differences between closely spaced lines can be measured more readily than for a single peak. When the meso phenyl groups are replaced by electron-releasing groups such as the eight ethyl substituents in H_2OEP or the *n*-propyl groups of H_2TPrP, both N 1s binding energies increase slightly at the same rate. The introduction of reduced carbons also causes the nitrogen binding energies to increase. However, in this case the binding energies associated with the unprotonated nitrogen peak increase at a greater rate than the protonated nitrogen peak.

The second class of compounds is illustrated in Figure 2 by AgTPP. This class consists of the metalloporphyrins which include the magnesium, zinc, cobalt, copper, nickel, and silver complexes of the tetraphenylporphyrin dianion, i.e., MgTPP, ZnTPP, CoTPP, CuTPP, NiTPP, and AgTPP. The pertinent binding energies for these complexes are summarized in Table II. In fitting the nitrogen peaks we find two subclasses within this set which are distinguished by differences in the shape of the N 1s peak. The peaks associated with MgTPP, ZnTPP, and NiTPP can all be fit with symmetric Guassian peak shapes. However, the N 1s peaks of CuTPP, CoTPP, and AgTPP require a Gaussian peak which is skewed to higher binding energy. Note that magnetic measurements show that MgTPP, ZnTPP, and NiTPP are diamagnetic[13] while CuTPP, CoTPP, and AgTPP are paramagnetic.[14] The Mg 1s spectrum of MgTPP was not obtained due to the poor cross section of this level. Upon prolonged exposure to the x-ray flux the nitrogen spectra changed from the single line characteristic of MgTPP to the double peaks more characteristic of H_2TPP. This demetalization was much less pronounced in samples prepared in the instrument drybox. No decomposition in the other complexes was noted. All of the metal binding energies could be fit with symmetric Gaussian peaks and showed no evidence of skewing.

The third class of compound is illustrated by the AgTPC nitrogen spectrum shown at the top of Figure 2. This class of reduced porphyrins includes the metal complexes of tetraphenylchlorin with magnesium, zinc, cobalt, copper, nickel, and silver. These complexes, MgTPC, ZnTPC, CoTPC, CuTPC, NiTPC, and AgTPC, all have the common feature that the nitrogen spectra can be deconvoluted into two peaks with an approximately 3:1 area ratio. The pertinent binding energies of these complexes as well as the separation between the peak maxima are listed with the corresponding porphyrin complexes in Table II. Two subclasses are also observed in this grouping, depending on whether the central metal ion is diamagnetic or paramagnetic. The diamagnetic complexes have a major nitrogen peak with a binding energy equal to the N 1s binding energy in the corresponding porphyrin complex. The smaller peak has a maximum shifted approximately 0.85 eV to higher binding energy. From the area ratio of approximately 3:1 we assign the major peak as the one arising from the three unreduced pyrrole nitrogens and the shifted peak as arising from the nitrogen on the reduced pyrrole ring. The second subclass is populated by the paramagnetic complexes which show a smaller peak shifted approximately 1.8 eV to higher binding energy (see Table II). The separation is twice that found in the diamagnetic compounds. The magnesium metal binding energy was again not recorded due to the poor signal to background counting ratio caused by the low core level cross section of the Mg 1s level. All XPS peaks arising from the metal ion showed no evidence of asymmetry.

Discussion

I. Free Bases. To determine the effect of ring reduction on the N 1s binding energies without the complication of a

Table III. Ir N–H Stretching Frequencies in Bromoform, KBr, and Nujol

Compd	Bromoform	KBr	Nujol	Ref
H_2P		3311.1 (±0.5)	3350 (±5)	14, 16
H_2TPrP	3325.2 (±0.5)			14
H_2TPP	3323.6 (±0.5)	3318.0 (±0.5)		14
H_2TPC		3343.9 (±0.5)		14
p-OCH_3			3370 (±5)	16
p-CH_3			3340 (±5)	16
p-Cl			3360 (±5)	16
p-NO_2			3360 (±5)	16

central metal ion, the free bases of H_2OEP, H_2TPrP, H_2TPP, H_2TPC, and H_2TPBC were studied. The interpretation of the XPS binding energies for these or any other system requires consideration of not only the initial or ground-state molecular properties but also the effect of electronic relaxation on the final photoionized core hole state. Changes in the initial-state configuration affect the measured binding energy through bond polarization caused by inequalities in the atomic or group electronegativities. Electron-withdrawing effects of fluoro or formyl substituents, for example, induce increases in the binding energy of the atoms in the substituted molecule. Relaxation in the final state affects the measured binding energy through the stabilization of the core hole remaining after photoionization. Less chemical information is available to assess the importance of final-state effects, although strong evidence is surfacing indicating that easily polarizable substituents can more effectively respond to the presence of the core hole. For example, the size of the alkyl substituent on various alcohols measured in the gas phase could be correlated with the magnitude of the relaxation effect.[42]

Since our main interest in studying binding energies of core electrons is to infer structural information about the ground state, we are faced with the perplexing chore of evaluating the magnitude of these final-state differences. For the unreduced free bases H_2OEP, H_2TPrP, and H_2TPP, for example, the ethyl and *n*-propyl substituents are generally thought to be electron releasing compared to the phenyl groups, but the N 1s values of H_2TPP are found at slightly lower binding energy signifying, in ground-state terms, the nitrogens have attained a small, additional electron density. It is tempting to unravel this dichotomy by invoking final-state effects. The relaxation energy for H_2TPP might be larger than that for H_2OEP or H_2TPrP if the phenyl rings are in resonance with the macrocycle's π system. ESR measurements on $Cu^{II}TPP$[13] and copper(II) tetrakis(p-chlorophenyl)porphyrin[11] have shown that the electron can delocalize over the meso phenyl groups, thereby increasing the effective size of the molecule. There is some difficulty with this interpretation. The N–H stretching frequencies as determined from the infrared spectra of porphyrin free bases and substituted porphyrin free bases also show the same ordering as the XPS spectra, as shown for the porphyrin free bases, H_2TPrP and H_2TPP, in Table III. Substituting the para positions of H_2TPP with electron-withdrawing groups also shifts the stretching frequencies to higher values. The increase in frequency indicates that the nitrogen electrons are more firmly held in H_2TPrP than in H_2TPP and is in direct agreement with the XPS results suggesting that the nitrogens do have a lower electron population.

Other arguments also support the interpretation of these XPS spectra in terms of ground-state properties. All of the porphyrins to be considered will be derivatives of H_2TPP and, therefore, should have nearly the same relaxation energy. Also, there is no difference between the N 1s binding energies of metalloporphyrins and the N 1s binding energies arising from the nitrogens located on rings I–III of the corresponding metallochlorins. This would indicate that the difference in the relaxation energies is within the experimental uncertainty of the measurement. For the remainder of this paper, then, primarily ground-state effects will be considered in our discussion.

Table IV. Total Electron Densities of Porphyrins and Reduced Porphyrins

Compd	N1	N2	N3	N4	Ref
Porphyrin dianion	1.923	1.923	1.923	1.923	43
Chlorin dianion	1.926	1.924	1.926	1.391	43
Bacteriochlorin dianion	1.928	1.403	1.928	1.403	43
Porphyrin free base	1.60	1.32	1.60	1.32	44
Chlorin free base	1.60	1.31	1.60	1.26	44
Bacteriochlorin free base	1.60	1.23	1.60	1.23	44

We turn our attention next to the changes in N 1s peaks on reduction of H_2TPP first to H_2TPC and further to H_2TPBC. Note that, as shown in Table I, the binding energies of both nitrogen peaks increase by up to 0.6 eV and the splitting decreases slightly by 0.2 eV as electron-releasing groups are added to the porphine skeleton. Thus, the experimental evidence suggests that reduction of the β carbons reduces the electron density of the nitrogens and results in an increase in the binding energy of the N 1s peaks. We can compare these observations to the molecular orbital calculations as performed by Gouterman et al.[43] and by Knop and Fuhrhop[44] which are reproduced in Table IV. Although the calculations were performed on compounds not exactly matching the free bases reported here, the dianion results of Gouterman do show the dramatic reduction in the total electron population on N4 caused by the reduction of the β carbons of ring IV. Furthermore, the calculations show a decrease in the differences between the electron populations of N1 and N4 of the chlorin dianion (0.535) and between those of N1 and N4 (0.525) of the bacteriochlorin anion. However, the calculations also show the electron population on N1 increasing when comparing the chlorin dianion and the bacteriochlorin dianion which is contrary to the XPS experimental observation. The calculations of Knop and Fuhrhop[44] on the free bases again show a reduction in charge density on N4 with the reduction of the β carbons of ring IV, followed by a smaller decrease in N4 with the further reduction of chlorin at ring II to bacteriochlorin. Note that three different peak positions are predicted although two of them are clearly too close to be experimentally resolved. This result matches the pattern observed in the XPS spectra and is consistent with the notion of considering the reduced β carbons to be electron withdrawing. These calculations, however, do not predict a decrease in the N 1s splitting upon reduction. Thus, although neither MO calculation exactly predicts the binding energy pattern, some features of the theory do correlate with the measured values. Even better agreement may be possible with a calculational method which does not ignore σ polarization and two-electron terms.

There is additional evidence supporting the identification of the reduced β carbons as decreasing the nitrogen electron density, as illustrated by the N–H stretching frequencies listed in Table III. Clearly the H_2TPC N–H stretching frequencies are larger than those of H_2TPP corresponding to a stronger N–H bond. This statement is equivalent to saying H_2TPC has a decreased basicity and a lower electron density on the nitrogen. Further evidence supporting the XPS binding energy patterns is derived from photometric titrations of porphyrin free bases.[45] These experiments show decreased basicity for the chlorin compared to that for the corresponding porphyrin. This fact again indicates that the electrons are more tightly held by the nitrogens in the reduced porphyrins. This effect corresponds to the higher binding energies measured by XPS and agrees with other studies relating acidity equilibria and XPS binding energies.[46] We also note that an earlier paper

Table V. Net Electron Densities of Metal Ions and Nitrogen Atoms in Metalloporphyrins and Metallochlorins

	Porphyrin		Chlorin			
Metal	Net metal	Net nitrogen	Metal	"Porphyrin" nitrogen	"Chlorin" nitrogen	Sepn
Mg	+0.59		+0.597	−0.212	−0.167	0.046
Zn	+0.40	−0.185	+0.402	−0.199	−0.153	0.046
Co	+0.34	−0.182				
Cu	+0.28	−0.182	+0.273	−0.196	−0.161	0.035
Ni	+0.30	−0.188	+0.275	−0.192	−0.158	0.034

by Falk et al.[39] shows the same pattern of binding energies for free bases derived from natural porphyrins and chlorins. However, the compounds used had different and complex substituents precluding the assignment of the cause of the increase of the overall binding energy and the decrease of the peak separation on ring reduction.

In summary it seems clear that the result of ring reduction is the development of an asymmetric center of charge withdrawal which reduces the electron density of the four nitrogens. The effect is largest with the unprotonated nitrogens of rings II and IV but is also evident with the nitrogens on rings I and III.

II. Metalloporphyrins. We next consider the effects of replacing the two protons of the free bases with various metal ions, increasing the symmetry from D_{2h} to D_{4h}. The four pyrrole nitrogens become equivalent with the nitrogen doublet in the free-base spectra, collapsing into a single metallonitrogen peak. A similar spectral simplification has also been reported for uv–vis spectra of porphyrins.[2–4] The position of the single peak is found between the positions where the two free-base peaks would be located and is shifted from the midpoint of the free-base spectra to a binding energy depending on the identity of the central metal ion.

In addition to increasing the symmetry of the molecule, the replacement of the free-base protons by a metal ion also introduces an electron-withdrawing center into the molecule which polarizes the σ-orbital network of the porphyrin. The polarization is produced through the donation of σ-electron density to the metal ion through the nitrogen atoms to reduce the metal's net positive charge. The magnitude of this polarization is sufficient so that reduction in the electron population at the periphery is large enough to increase the β–β carbon bonds as measured by x-ray crystallography. The increase is quite dramatic when comparing the 1.350-Å length found in NiTPP with the 1.379-Å length found in $Sn^{IV}TPPCl_2$.[20] Although the effect of σ donation on the metal's electronic population is of great interest, it is difficult to assess with XPS because it is impossible to measure the binding energy of the neutral metal ion in the same matrix but without the σ donation operating. However, it is possible to measure the effect of the metal ion on the ligand by changing the metal and following subsequent changes in the N 1s binding energies.

From the entries in Table II, significant differences can be observed between the N 1s binding energies for the porphyrin ligand attached to several different metal ions. We have found a general correlation between these values and the metal ion electronegativity[47,48] as shown in Figure 3. The electronegativity parameter is a measure of the ability of an atom to draw electron density toward itself in a covalent bond and thus should correspond to a decrease in the electron density on the nitrogen atoms, as observed. The charge densities of the central metal ion and of the central nitrogens have been estimated from an extended Hückel molecular orbital treatment as shown in Table V.[5] It is interesting to note that the N 1s binding energy increases as the net calculated total charge on the metal ion decreases. However, there appears to be no correlation with the measured nitrogen binding energy and the calculated net charge on the nitrogen.

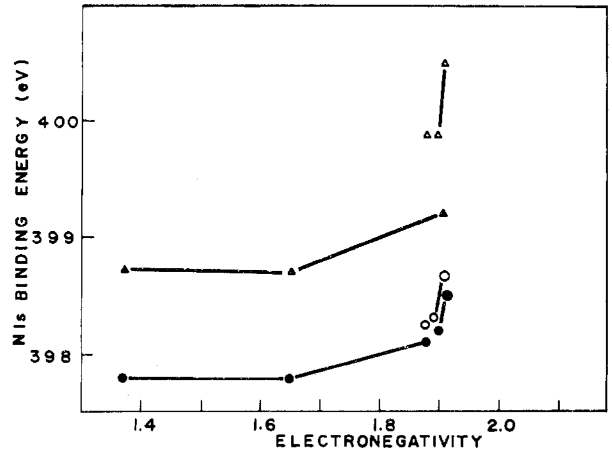

Figure 3. N 1s binding energies of metalloporphyrins and -chlorins (electronegativity values used: Mg, 1.37; Zn, 1.65; Co, 1.88; Cu, 1.90; Ni, Ag, 1.91): ●, porphyrin nitrogen and "porphyrin" nitrogens of diamagnetic metallochlorins; ○, "porphyrin" nitrogens of paramagnetic metallochlorins; ▲, "chlorin" nitrogens of diamagnetic metallochlorins; △, "chlorin" nitrogens of paramagnetic metallochlorins. See text for further explanation.

The distinction in peak shape between paramagnetic and diamagnetic species is somewhat surprising. As reported earlier the N 1s peak shape is dependent on the presence or absence of the odd electron. The nitrogen 1s peaks of the diamagnetic complexes can be fit very well with a symmetric Gaussian peak shape, but the paramagnetic molecules all have nitrogen peaks which are skewed to higher binding energy. Whether this asymmetry is due to final state effects such as multiplet splitting or electron "shake-up" cannot be unequivocally resolved, but the absence of any structure on the metal ion photoelectron peak casts doubt on this interpretation. Other spectral evidence points to possible complexities associated with ground-state electronic structure. For example, when odd d electrons are available for bonding, the spectra are shifted to the blue region and the first electronic transition is depressed.[2] Further in the metallochlorins discussed in the next section there is a distinct division in the behavior of the "chlorin" nitrogen peak with diamagnetic and paramagnetic complexes. It is this new splitting which now merits closer consideration.

III. Metallochlorins. Having established that ligand reduction produces an electron-withdrawing center in the previously symmetric porphyrin ligand and the metal ion replacement of the free-base protons both increases the symmetry of the molecule and provides a center of electron-withdrawing power, we combine these results to describe the metallochlorins. From the sample N 1s spectra in Figure 2 it is obvious that the metal ion does not increase the symmetry of the molecule to D_{4h} as in the metalloporphyrins. This is mirrored by the lack of simplification found in the uv–vis absorption spectra when changing from the free base to the metallochlorin.[8] Thus the spectra are composed of two overlapping peaks with area ratios ranging from 27:73 for ZnTPC to 21:79 for AgTPC. This corresponds approximately to the 1:3 peak area ratio expected if the three nitrogens attached to the unreduced ring have a different chemical environment from the nitrogen attached to the reduced ring. Differences in line shapes between the N 1s peaks of the different chlorins make deconvolution only an approximate procedure. In the cases reported here, we have used the peak shape of the corresponding porphyrin species to establish the line shape of the lower binding energy peak. The area of the high binding energy peak could then be determined by difference. The presence of two chemically distinct peaks is supported by additional theoretical and experimental evidence. Molecular orbital calculations show as discussed previously that the chlorin dianion has two types of nitrogens in a 3:1 area ratio in contrast to the porphyrin dianion which is fourfold degenerate.[43] This difference is maintained when the metal ion is introduced into the dianion chlorin as shown in Table V.

The observation of these differences in the charge densities has also been made experimentally with ^{15}N NMR in the natural magnesium chlorin, chlorophyll a, and its free-base derivative, pheophytin a.[24] The ^{15}N NMR spectra yield the same picture as the XPS data with the protonated nitrogens of pheophytin a, showing N1 and N3 as a pair of lines at low field and a more widely spaced pair at higher field which correspond to the unprotonated nitrogens, N2 and N4. This pattern reduces to the nearly equivalent nitrogen lines of chlorophyll a corresponding to N1, N2, and N3, with N4 split off to higher field. Although the NMR spectra provide qualitative support for the XPS measurements, it should be noted that quantitative agreement between the XPS binding energy and the NMR chemical shift is not expected. In a recent paper Gelius et al.[49] explored the relationship between XPS and NMR measurements and concluded that although the XPS binding energy was primarily dependent on the charge on an atom, the NMR shift was strongly affected by other factors. As shown in eq 1 the NMR average chemical shift,

$$\sigma_{\mathrm{A,av}} = \sigma_{\mathrm{AA}} + \sigma^{\mathrm{P}}_{\mathrm{AA}} + \sum_{\mathrm{B}\neq\mathrm{A}} \sigma_{\mathrm{AB}} + \sigma_{\mathrm{A,ring}} \qquad (1)$$

$\sigma_{\mathrm{A,av}}$, can be dissected into four terms. The first term is the diamagnetic shielding term which describes the ability of the spherically symmetric charge of the atom to screen the applied magnetic field and is the source of the charge dependence on the NMR shift. However, the magnitude of this effect is reduced by the paramagnetic shift term, $\sigma^{\mathrm{P}}_{\mathrm{AA}}$, which describes the degree of loss of spherical symmetry with the increase in molecular size. The final two terms are the interatomic shielding term, σ_{AB}, and the ring current shielding term, $\sigma_{\mathrm{A,ring}}$, which are self-explanatory. Because even in simple systems it is not possible to separate the diamagnetic and paramagnetic shielding terms, correlations between XPS binding energies and ^{11}B and ^{13}C NMR have been unsuccessful. In porphyrins the molecular size is much larger than in the cited examples and the π system predicts a large ring current to be present. This means quantitative correlation should be even less expected.

The effect of the metal ion electronegativity is illustrated in Figure 3 by plotting the XPS N 1s binding energy of the metallochlorins vs. the metal electronegativity. The role of the metal ion is similar to the metalloporphyrins in providing a central electronegative group, since the binding energies for the metallochlorins for N1, N2, and N3 parallel the increase of the metalloporphyrins. The plot also shows, however, that the paramagnetic and diamagnetic metal ions do not interact exactly the same with N4 and there is a small upward shift in the "porphyrin" nitrogens of the paramagnetic complexes. Whether this shift is due to final-state energy changes or to real differences in the N 1s charge densities is not clear. However, the "porphyrin" N 1s binding energies of the diamagnetic chlorins do coincide with the nitrogen binding energies of the corresponding porphyrins. The "chlorin" nitrogen peaks of the diamagnetic metallochlorins are found, as shown, about 0.9 eV higher in binding energy than the "porphyrin" nitrogen peak. The separation is relatively the same for Zn and Mg but decreases slightly for NiTPC. As shown in Table V, this is similar to the behavior predicted by the molecular orbital calculations by Zerner and Gouterman.[5] The "chlorin" nitrogen of the paramagnetic complexes is shifted approximately 1.7 eV from the "porphyrin" peak. Furthermore, the separation increases very slightly with increasing electronegativity. This signifies that the electron density on N4 is decreasing with an increase in the central metal electronegativity more rapidly than are the electron densities on the other three nitrogens.

The increase in separation between the "porphyrin" and "chlorin" peaks found in the paramagnetic metallochlorins is not predicted by the extended Hückel MO calculation listed in Table V. It is unfortunate that there are no other results from MO calculations for paramagnetic metallochlorins available to compare with the XPS binding energies. One cannot judge from the calculations on only one paramagnetic species whether the model will support the larger separation between the peak centers for the other paramagnetic metallochlorins or the slight increase in the size of separation with increasing electronegativity. However, the lack of agreement in the separation in the case of the copper chlorin may be due to the neglect of σ polarization and two-electron terms in the molecular orbital calculations, both of which are important in these types of interactions.[50] Also, the model molecule used for the chlorin macrocycle is formed by deleting the β carbons from ring IV as shown in Figure 1e.[51] Although correlations between the chlorins studied here and other spectral and theoretical results cannot be made due to the lack of these results, it is obvious the XPS binding energies predict that even though metallochlorins behave similarly to the corresponding porphyrins, there are some differences in the finer details. Furthermore, additional experiments should be carried out to determine the scope and magnitude of the differences in the properties of diamagnetic and paramagnetic porphyrins and chlorins illustrated above.

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Registry No. H_2OEP, 2683-82-1; H_2TPrP, 22112-75-0; H_2TPP, 917-23-7; H_2TPC, 2669-65-0; H_2TPBC, 25440-13-5; MgTPP, 25447-36-3; MgTPC, 53199-30-7; ZnTPP, 25447-11-4; ZnTPC, 14839-32-8; NiTPP, 14172-92-0; NiTPC, 59888-74-3; CoTPP, 14172-90-8; CoTPC, 59888-73-2; CuTPP, 14172-91-9; CuTPC, 52064-15-0; AgTPP, 14641-64-6; AgTPC, 59888-75-4.

References and Notes

(1) (a) Partially supported by a grant (GP-37017X) from the National Science Foundation. (b) Alfred P. Sloan Fellow, 1974–1976.
(2) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.*, **73**, 4315–4320 (1951).
(3) M. Gouterman, *J. Chem. Phys.*, **30**, 1139–1161 (1959).
(4) M. Gouterman, *J. Mol. Spectrosc.*, **6**, 138–163 (1961).
(5) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44–63 (1966).
(6) A. Treibs, *Ann. N.Y. Acad. Sci.*, **206**, 97–115 (1973).
(7) C. Weiss, *J. Mol. Spectrosc.*, **44**, 37–80 (1972).
(8) G. D. Miller and F. M. Heunnekens, *J. Am. Chem. Soc.*, **74**, 3974–3976 (1952).
(9) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2662–2669 (1963).
(10) D. Eastwood and M. Gouterman, *J. Mol. Spectrosc.*, **30**, 437–458 (1969).
(11) D. J. E. Ingram, J. E. Bennett, P. George, and J. M. Goldman, *J. Am. Chem. Soc.*, **78**, 3545 (1956).
(12) B. Roos and M. Sondbom, *J. Mol. Spectrosc.*, **36**, 8–25 (1970).
(13) J. Fajer, D. C. Borg, A. Forman, R. H. Felton, L. Vegh, and D. Dolphin, *Ann. N.Y. Acad. Sci.*, **206**, 349–354 (1973).
(14) J. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965).
(15) J. O. Alben, S. S. Choi, A. D. Adler, and W. S. Caughey, *Ann. N.Y. Acad. Sci.*, **206**, 278–295 (1973).
(16) L. J. Boucher and J. J. Katz, *J. Am. Chem. Soc.*, **89**, 1340–1345 (1967).
(17) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1338 (1956).
(18) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959).
(19) E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105–112 (1970).
(20) J. L. Hoard, *Science*, **174**, 1295–1302 (1971).
(21) M. S. Fisher, D. H. Templeton, A. Zalkin, and M. Calvin, *J. Am. Chem. Soc.*, **94**, 3613–3619 (1974).
(22) C. B. Storm, Y. Teklu, and E. Sokoloski, *Ann. N.Y. Acad. Sci.*, **206**, 631–640 (1973).

(23) J. J. Katz and T. R. Janson, *Ann. N.Y. Acad. Sci.*, **206**, 579–603 (1973).

(24) S. G. Boxer, G. L. Closs, and J. J. Katz, *J. Am. Chem. Soc.*, **96**, 7058–7066 (1974).

(25) L. D. Spaulding, C. C. Chang, N.-T. Yu, and R. H. Felton, *J. Am. Chem. Soc.*, **97**, 2517 (1975).

(26) T. G. Spiro and T. C. Strekas, *J. Am. Chem. Soc.*, **96**, 338 (1974).

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

(28) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, **92**, 3451–3459 (1970).

(29) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982–2991 (1970).

(30) F. J. Ryan, A. A. Bambara, and P. A. Loach, *Bioorg. Chem.*, **2**, 44–58 (1972).

(31) J.-H. Fuhrhop, *Angew. Chem., Int. Ed. Engl.*, **13**, 321–335 (1974).

(32) Nomenclature follows that of Hoard.[20]

(33) R. H. Felton, G. S. Owen, D. Dolphin, and J. Faher, *J. Am. Chem. Soc.*, **93**, 6332–6334 (1971).

(34) K. Kadish, D. G. Davis, and J.-H. Fuhrhop, *Angew. Chem., Int. Ed. Engl.*, **11**, 1014–1016 (1972).

(35) G. Peychal-Heiling and G. S. Wilson, *Anal. Chem.*, **43**, 550–556 (1971).

(36) M. V. Zeller and R. G. Hayes, *J. Am. Chem. Soc.*, **95**, 3855–3860 (1973).

(37) D. H. Karweik, N. Winograd, D. G. Davis, and K. M. Kadish, *J. Am. Chem. Soc.*, **96** 591–592 (1974).

(38) Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799–807 (1974).

(39) H. Falk, O. Hofer, and H. Lehner, *Monatsh. Chem.*, **105**, 366–378 (1974).

(40) K. Siegbahn et al., *Science*, **176**, 245 (1972).

(41) K. S. Kim and N. Winograd, *Surf. Sci.*, **43**, 625–643 (1974).

(42) R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.*, **96**, 5299 (1974).

(43) M. Gouterman, G. H. Wagniere, and L. C. Snyder, *J. Mol. Spectrosc.*, **11**, 108–127 (1963).

(44) J. V. Knop and J.-H. Fuhrhop, *Z. Naturforsch., B*, **25**, 729–734 (1970).

(45) S. Aranoff, *J. Phys. Chem.*, **62**, 428–431 (1958).

(46) J. S. Jen and T. D. Thomas, *J. Am. Chem. Soc.*, **97**, 1265 (1975).

(47) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745–786 (1955).

(48) J. W. Buchler, L. Puppe, K. Rohback, and H. H. Schmeehage, *Ann. N.Y. Acad. Sci.*, **206**, 117–137 (1973).

(49) U. Gelius, G. Johansson, H. Seigbahn, C. J. Allan, D. A. Allison, and K. Seigbahn, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 285–295 (1972–1973).

(50) K. S. Kim, private communication.

(51) M. Gouterman, private communication.

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Concerning the Thermochromic Mechanism of Copper(II) and Nickel(II) Complexes of *N*,*N*-Diethylethylenediamine[1]

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The thermochromic mechanism of several Cu(II) and Ni(II) complexes of the type $M(dieten)_2X_2$, where dieten = *N*,*N*-diethylethylenediamine and X = inorganic anion, has not been clearly established. Pressure and thermal studies in the electronic and infrared region (mid-infrared and far-infrared) have been made. In the electronic region, the "d–d" transitions shift red with an increase in temperature for both Cu(II) and Ni(II) complexes. With pressure these transitions are toward the red with Cu(II) complexes and toward the blue with Ni(II) complexes. Mid-infrared data are indicative of axial interaction occurring with an increase in temperature and the lack of interaction with pressure increases. Although many factors are involved in determining these differences and anion and steric effects are important, the dominant factor appears to be the distortion of the tetragonal metal atom environment and axial interaction between the anions and the $M-N_4$ plane.

Some of the copper(II) and nickel(II) complexes of *N*,*N*-diethylethylenediamine (dieten) of the type $M(dieten)_2X_2$, where X is an anion, have demonstrated reversible thermochromic behavior.[3–8] Considerable physical studies have been made on these compounds. For example, temperature-dependent infrared, far-infrared, electronic spectra,[6] magnetic,[6] ESR,[7] and calorimetric measurements have been reported.[8–10] The visible absorption bands for the copper complexes demonstrate an abrupt red shift with a temperature increase. In the nickel complexes a similar red shift is observed, and except for the compounds containing BF_4^- or ClO_4^-, the shift increases regularly with a temperature rise. The two modes of behavior have been designated by Paoletti and co-workers as discontinuous and continuous thermochromism.[8] From these studies Lever has concluded that the mechanism for the thermochromism displayed by these complexes was associated with the distortion of the tetragonal metal atom environment and the axial interaction between the anions and the $M-N_4$ plane.[6]. It seems more than likely that there are other factors which could have a major role in delineating the mechanism. One such factor could be steric effects in complexes of substituted ethylenediamine containing bulky alkyl groups. By combining both pressure and thermal measurements and studying any changes observed in the electronic and infrared spectra, the relative importance of such factors may be better defined. This paper reports on the results of such studies and presents a suggested interpretation which supports Lever's conclusion.

Experimental Section

Materials. The preparation of the complexes has been previously reported.[8] Since some of the complexes were deliquescent, only desiccated material was used in the physical studies.

Spectral Measurements. For the region between 4000 and 650 cm^{-1} a Beckman IR-12 and the diamond anvil cell (DAC) were used.[11] For the region <650 cm^{-1}, measurements were made with a Perkin-Elmer Model 301 and a DAC.[12] In both instruments a 6X beam condenser was necessary.[11–12] Electronic spectra were recorded in a Cary 14 spectrophotometer interfaced with a special beam condenser.[13] Both ambient and nonambient spectra were obtained. For spectra recorded at elevated temperatures, a chromel–alumel thermocouple (with an ice junction as reference) was used to measure temperatures.

Results and Discussion

A. Electronic Region. Table I compares temperature, pressure, and environmental effects on the electronic transitions of $Cu(dieten)_2X_2$ complexes. Table II lists the comparison of temperature and pressure effects on the electronic transitions of $Ni(dieten)_2X_2$. It may be observed that with increasing temperature a red shift (toward lower energy) in the visible absorption occurs for both series of complexes, and thermochromism occurs with a conversion to a weakly tetragonally distorted octahedra. Thus a red shift may be viewed as the tendency of the complex to go toward an octahedral environment (increased axial interaction of the anions with the MN_4 plane) and a tendency toward thermochromism.

When the complexes are subjected to high external pressures, a strong anion dependency is noted. In the copper complexes small red shifts occur for the nitrate, perchlorate, and BF_4^- anions, but no color changes occurs. For the nickel complexes a strong anion effect is also observed, and the shift in the "d–d" transition appears to progress toward the blue region. However, as the anion becomes progressively softer (polarizable) the amount of blue shift becomes smaller, and for the complex containing the iodide anion a red shift occurs.