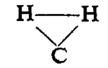
Furthermore, observation of $C_2H_7^+$ at these conditions implies that the decomposition[14]

$$C_2H_7^+ \longrightarrow C_2H_5^+ + H_2 \qquad (27)$$

has an activation energy which is probably greater than that for H_2 elimination from $B_2H_7^+$. Low-temperature ion–molecule reactions in C_2H_6 produce a species of m/e 59 which appears to be formed by the reaction $C_2H_5^+ + C_2H_6 \rightarrow C_4H_{11}^+$ (1972, unpublished work by this laboratory).

This is quite analogous to the reaction between $B_2H_5^+$ and B_2H_6. However, at normal source temperatures neither $C_4H_{11}^+$ nor $B_4H_{11}^+$ is observed within the limits of our sensitivity.

Proposed structures for $B_2H_7^+$ and $B_4H_{11}^+$ are illustrated in Figure 11. A number of other configurations are possible and theoretical calculations may help resolve these. The structure of $B_2H_7^+$ is suggested by analogy with CH_5^+, which is now believed to have C_s configuration consisting of three "normal" C–H bonds and one three center bond.



The structure for $B_4H_{11}^+$ is assumed to be a composite of $B_2H_5^+$ and B_2H_6 with four bridge hydrogen bonds and seven terminal B–H bonds. The small value of ΔH for formation of $B_4H_{11}^+$ from $B_2H_5^+$ and B_2H_6 suggests no significant net change in structural features of the reactants and product.

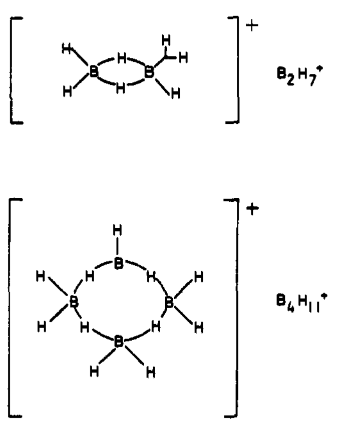


Figure 11. Possible structures for $B_2H_7^+$ and $B_4H_{11}^+$.

Acknowledgment. We are grateful for support by the Army Research Office—Durham, N. C., and the National Science Foundation (Grant GH 33637) through the Materials Science Center, Cornell University.

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[14] The ΔH has been estimated to lie between 0 and 9 kcal/mol. J. L. Franklin and F. H. Field, "Electron Impact Phenomenon and Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957.

X-Ray Photoelectron Spectroscopic Studies on the Electronic Structures of Porphyrin and Phthalocyanine Compounds

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Abstract: We have measured the nitrogen 1s binding energies and some metal binding energies of porphyrin and phthalocyanine compounds by X-ray photoelectron spectroscopy. We find that this technique yields interesting new data. In particular, we find two kinds of nitrogen in tetraphenylporphine free base, differing in charge by about 0.2 e. We find the nitrogens of most metalloporphyrins to be similar to those of porphine base which lack protons. We find the two kinds of nitrogen in metal phthalocyanines to be identical with photoelectron spectroscopy. Finally, we find that the iron in the oxidized and reduced forms of iron porphyrin differ in charge by some 0.44 electron charges. On the whole, our results compare well with the theoretical predictions of Gouterman and coworkers.

It is already well known that X-ray photoelectron spectroscopy offers the possibility of measuring the charge distribution in molecular systems.[1-3] It thus provides a unique view of the electronic structure of a system, a view which is close to the basic theoretical ideas we use in discussing molecules. We have been applying the technique to various porphyrin and phthalocyanine compounds and we report some of our results herein.

It is unlikely that we shall be able to obtain a complete charge distribution for one of these molecules in the foreseeable future and, in this report, we shall restrict ourselves primarily to discussing the charges on the nitrogen atoms in the various compounds.

Porphyrin and phthalocyanine compounds have received a great deal of attention, partly because of their relevance to various biological systems, but most of the techniques heretofore available provide either information which is only indirectly related to the ground-state electronic structure, or information about only a portion of the electronic structure. X-Ray crystal-

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[1] K. Siegbahn, *et al.*, "ESCA–Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksell, Uppsala, Sweden, 1967.

[2] J. M. Hollander and D. A. Shirley, *Annu. Rev. Nucl. Sci.*, **20**, 435 (1970).

[3] M. E. Schwartz, J. D. Switalski, and R. E. Stronski in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 605.

lographic studies are examples of the first kind of study,[4] and examples of the second kind are nuclear magnetic resonance,[5] electron paramagnetic resonance,[6] and Mössbauer spectroscopy.[7] The latter techniques often provide detailed information about certain aspects of the electronic structure, such as the distribution of unpaired electrons, but nothing at all about the gross electronic structure or total electron density distribution.

Photoelectron spectroscopic studies may be expected to complement the other techniques by providing information about the gross electronic structure, however crude such information may be at the present. We report here not only the binding energies of the nitrogen K shells of various porphyrin and phthalocyanine compounds but also the binding energies of the same shell in a few simple salts, most of which have been determined previously by Hendrickson and Jolly.[8] We did this because the accepted method of standardizing X-ray photoelectron spectra of insulators has changed since the work of Hendrickson and Jolly, although our results differ little from theirs.

Experimental Section

All X-ray photoelectron spectra were obtained using a Varian IEE-15 photoelectron spectrometer, which is a retarding potential, electrostatic instrument. We standardized our spectra by evaporating a thin gold layer over the samples under vacuum, using a separate deposition unit consisting of a bell jar which had feedthroughs for a rotatable sample support rod and for an evaporator, which consisted of a length of tungsten wire onto which gold beads had been melted. The standard sample holder of the Varian spectrometer is a cylindrical aluminum slug, and we mounted our samples on it using double-sided Scotch tape.

Studies of the X-ray photoelectron spectra of insulators which have received thin gold layers suggest that, although the layer does not necessarily bring the sample into electrical contact with the spectrometer, the sample maintains electrical contact with the gold film.[9] One may, thus, eliminate the effects of charging of the sample by correcting the binding energy of one of the gold levels to some accepted value and applying the same correction to the binding energies of levels of the sample. We assumed that the N_{VI} level of Au($4f_{5/2}$) was bound by 87.0 eV.

It was our observation that the photoelectron spectra of the salts which we studied showed little evidence of charging. The spectra were sharp. Good spectra could be obtained without effort, and the reproducibility of the spectra was good. This is consistent with Hamill's observation that all salts which he has studied as thin films *in vacuo* conduct injected charge readily.[10] On the other hand, the porphyrin and phthalocyanine compounds we studied were singularly difficult to handle. These compounds charge up readily, even upon grinding, and we had great difficulty in getting reproducible spectra or even usable spectra. We finally found we could get reproducible, sharp spectra by using the thinest possible layer of sample. We also tried to run thin films of sample, prepared by evaporation of solutions directly on the Al sample holder, but our results were poor in that they disagreed with reproducible results from the former method. We feel that the problem lies in the fact that most of the gold film deposited on the latter samples may have lain on uncovered Al rather than on sample, yielding an erroneous calibration. It is known that, if only part of the sample holder is covered, one gets a splitting of the photoelectron peaks from a gold film.

Of the compounds we studied, the inorganic salts are all readily available and commercial sources of reagent-grade compounds were used. All the phthalocyanine compounds were gifts of Professor Bro. Columba Curran, C.S.C., and had been prepared by Dr. Sr. Mary Dismas O'Rourke,[11] as had been the zinc and tin porphyrin compounds. We prepared tetraphenylporphine (abbreviated H_2TPP) and chlorotetraphenylporphinatoiron(III) (abbreviated $Fe^{III}ClTPP$) by the method described by Adler, *et al.*[12] The μ-oxo-bis[tetraphenylporphinatoiron(III)] (abbreviated $(FeTPP)_2O$) was prepared according to Caughey's prescription.[13] The conjugate acid of tetraphenylporphine (abbreviated H_4TPP^{2+}) was prepared by adding 12 *N* HCl to a solution of H_2TPP in chloroform. The product fell out immediately. The hemin chloride we used was obtained commercially [Nutritional Biochemicals Corp., Cleveland, Ohio]. We prepared the dipiperidine hemochromes of hemin and of FeTPP by refluxing the corresponding ferric chlorides in piperidine, taking care to exclude air.[14] The cobalt porphyrins were gifts from Professor G. Robert Scheidt.

Results

Our data are summarized in Table I, which contains all the binding energy data we have obtained on N 1s binding energies, and in Table II, which contains a miscellany of binding energies of other elements in the porphyrin and phthalocyanine compounds and, also, a few other binding energies which may serve as references for some of the data from porphyrins and phthalocyanines. The binding energies were all, except as noted, obtained from a visual inspection of the data, a procedure which we find to be as reliable as least-squares analysis of the data if there are no overlapping peaks. Overlapping peaks were resolved by using a

Table I. N 1s Binding Energies (eV) in Various Compounds, Referred to Au N_{VI} = 87.00 eV

	Simple Reference Compounds		
KCN	397.8	$K_3Cr(CN)_5NO \cdot 2H_2O$	397.6
$NaNO_2$	402.8		400.0
$NaNO_3$	405.8	$Na_2Fe(CN)_5NO \cdot 2H_2O$	397.2
NH_4NO_3	400.9		402.3
	405.8		
	Porphyrins		
H_2TPP	397.2	$Fe^{III}ClTPP$	398.6
	399.1	$[Fe^{III}TPP]_2O$	397.3
H_4TPPCl_2	399.1	$Fe^{III}ClProto$[b]	397.3
$Zn^{II}TPP$	397.2	$Sn^{IV}Cl_2TPP$	398.2
$Zn^{II}TPyP$[a]	397.3	$Fe^{II}(pip)_2TPP$	397.7
$Co^{II}TPP$	397.2		
$Co^{II}(NO)TPP$	397.7		
	400.4		
	Phthalocyanines		
H_2Pc	397.9[c]	$Sn^{IV}Cl_2Pc$	398.3
Na_2Pc	397.3	$Sn^{IV}(Pc)_2$	397.6
$Cu^{III}Pc$	397.5		
$Sn^{IV}F_2Pc$	398.0		

[a] TPyP = tetra(4-pyridyl)porphine. [b] Hemin chloride. [c] Broad unresolved peak.

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[4] Recent reviews of X-ray studies of porphyrins and phthalocyanines may be found in J. L. Hoard, *Science*, 174, 1295 (1971), and E. Fleischer, *Accounts Chem. Res.*, 3, 105 (1970).

[5] R. G. Schulman, S. H. Glarum, and M. Karplus, *J. Mol. Biol.*, 57, 93 (1971), contains data on CN complexes of heme compounds and a detailed analysis. See also R. J. Kurland, R. G. Little, D. G. Davis, and C. Ho, *Biochemistry*, 10, 2237 (1971).

[6] W. E. Blumberg, J. Peisach, B. A. Wittenberg, and J. B. Wittenberg, *J. Biol. Chem.*, 243, 1854 (1968); W. E. Blumberg and J. Peisach, *Advan. Chem. Ser.*, No. 100, 271 (1971).

[7] G. Lang, T. Asakura, and T. Yonetani, *Proc. Phys. Soc., London* (*Solid State Phys.*), 2246 (1969).

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

[9] R. G. Steinhardt, J. Hudis, and M. L. Perlman, ref 3, p 557.

[10] K. Hiraoka and W. H. Hamill, *J. Chem. Phys.*, to be submitted for publication.

[11] M. D. O'Rourke, Ph.D. Thesis, University of Notre Dame, 1968.

[12] (a) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 32, 476 (1967); (b) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970).

[13] N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, 8, 534 (1969).

[14] L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, 6, 1720 (1967).

Table II. Binding Energies (eV) of Various Core Levels of Interest to the Analysis of Porphyrins and Phthalocyanines

$Co^{II}TPP$		$K_4Fe(CN)_6 \cdot 3H_2O$	
Co $2p_{3/2}$	778.8	Fe $2p_{3/2}$	707.2
$Co^{II}(NO)TPP$		N 1s	396.7
Co $2p_{3/2}$	779.3	$Na_2Fe(CN)_5NO \cdot 2H_2O$	
$Co(acac)_2$		Fe $2p_{3/2}$	709.6
Co $20_{3/2}$	780.0	$Fe^{III}ClTPP$	
$K_3Co(CN)_6$		Fe $2p_{3/2}$	711.9
Co $2p_{3/2}$	781.2		
N 1s	397.3		
$K_3Fe(CN)_6$		$Fe^{II}(pip)_2TPP$	
Fe $2p_{3/2}$	708.5	Fe $2p_{3/2}$	707.5
N 1s	396.6	$Fe^{II}ClProto$	
		Fe $2p_{3/2}$	710.5
		$Fe^{II}(pip)_2Proto$	(706.1)[a]
		Fe $2p_{3/2}$	

[a] See text for significance of parentheses.

routine due to Mr. Conrad Naleway, which performs a least-squares fit of the data to a function consisting of a sloping background, a Gaussian or Lorentzian curve for each peak, and a tail on the high-energy side of the peak. The reported binding energies have an uncertainty of at least ±0.2 eV, based on our experience in running duplicate samples on our spectrometer at different times.

A few points are perhaps noteworthy. One is that the N 1s peak in $Zn^{II}TPyP$ was quite sharp, indicating that the pyrrole and pyridine nitrogens have quite the same binding energies. The N 1s peak of $Cu^{II}Pc$ was also very sharp, in contradistinction to the N 1s peak from the Pc neutral ligand.

Discussion

Before discussing our data, it is well to outline the current knowledge of the interpretation of binding energies measured using samples which are insulating solids. Two sources of uncertainty in such measurements are known. Firstly, the sample may collect charge, which causes all binding energies to be shifted by the electrostatic potential of the sample. One assumes that he corrects for sample charging by referring all binding energies to the binding energy of a core level in a thin film of gold evaporated onto the sample. There is reason to believe this assumption to be correct,[9] but it is not known that such a method may be applied successfully to all samples. In point of fact, we find that the method must be used with great care, when applied to our samples. We have said already that our samples charge up readily. We find that if the sample is too thick, or the gold layer does not cover the whole sample, our results are worthless. Also, if the sample does not cover the support well we get results which deviate from consistent sets of results from samples which do cover the support well. This is, presumably, because much of the gold lies on the support, not the sample.

A second source of uncertainty in measurements on insulating solids is often called the solid-state effect. This name refers to a putative difference between binding energies measured on a gaseous system and those values obtained from the same system in the solid state. There are a number of possible contributions to such an effect, the most obvious of which is the potential at an atomic site due to other molecules in the solid. The experimental evidence for this effect seems rather small. Siegbahn and coworkers[15] have noted shifts in comparing spectra of some molecules in the gas phase and in condensed phases, but they did not resolve them into the contributions from charging and from the solid-state effect. There is a certain amount of evidence which suggests that the solid-state effect is of minor consequence in determining differences of binding energies among different samples. One piece of evidence is the general success in correlating binding energies measured on solids with predictions obtained from calculations on isolated molecules, of which there are already many examples in the literature.

Aside from uncertainties which arise in associating a binding energy measured on a solid with the binding energy of a free molecule, there are ambiguities in relating binding energies to other molecular properties of more direct interest, such as charge densities. The latter problem has received a very large amount of attention. It seems inappropriate to review that area in this paper, so we refer the reader to some recent reviews which cover the topic,[2,3] and merely state here the position we propose to take.

We shall assume that a change in valence electron density of one electron causes a change in binding energy of 10 eV for all core levels of all elements. The plausibility of such an assumption has been pointed out by Hollander and Shirley.[2] This is undoubtedly a crude assumption, but it should suffice primarily because the compounds we study are probably not very ionic, so there is no great buildup of charge anywhere in the system.

It follows, from the argument of the preceding several paragraphs, that some of our results are more reliable than others. In particular, results which do not depend on a comparison of different compounds but which involve only comparison of two or more inequivalent atoms of the same element in one compound are more reliable. The most reliable conclusions of our work are, then, the following. (1) There are two kinds of nitrogen in tetraphenylporphine, which are presumably those with and without hydrogens attached. We shall call these, henceforth, the aza nitrogens and the pyrrole nitrogens. The question of the nature of the nitrogens in porphine free bases has received much attention.[16] Our results rule out any structure with hydrogen bridges, yielding equivalent nitrogens but, of course, do not rule out intramolecular hydrogen bonding of some sort. We find an electron density difference of 0.19 e between the two nitrogens, with the aza, presumably, more positive. (2) The two kinds of nitrogen in $Zn^{II}TPyP$ have essentially the same binding energy. The nitrogen 1s photoelectron line is a little broad, though, and the two nitrogens may differ by 0.2 or 0.3 eV in binding energy. The charge on nitrogen in pyridine, from CNDO calculations, is −0.166 electron.[8] The pyrrole nitrogens of $Zn^{II}TPyP$ are expected, thus, to have the same charge, to within a few hundredths of an electron. (3) The compound, $Fe^{II}(pip)_2TPP$, shows only one N 1s binding energy. It follows that the pyrrole nitrogens and the nitrogen of piperidine in this compound must have essentially

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(15) K. Siegbahn, *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

(16) A recent discussion, with citations to the earlier literature, may be found in A. M. Schaeffer and M. Gouterman, *Theor. Chim. Acta*, **25**, 62 (1972).

identical binding energies. (4) The two kinds of nitrogen in copper phthalocyanine [$Cu^{II}Pc$], in several tin phthalocyanine dihalides, $Sn^{IV}X_2Pc$ ($X^- = F^-, Cl^-, Br^-$), and in $Sn(Pc)_2$ are identical from the point of view of X-ray photoelectron spectroscopy. There is no evidence for more than one nitrogen 1s binding energy in any of these compounds. On the other hand, in phthalocyanine free base the nitrogen photoelectron peak is quite broad, though unresolved, and the spread in binding energies among the various nitrogens must be about 2 eV.

The less reliable information, coming from comparison of binding energies in different compounds, is summarized, for the most part, by Table III. We have expressed the information as charges, assuming the charge on nitrogen in pyridine to be −0.17, as mentioned previously.

Table III. Charges on Nitrogen in Various Porphyrin and Phthalocyanine Compounds

$Zn^{II}TPyP$		$Sn^{IV}Cl_2Pc$	−0.07
Pyrrole	−0.17	$Fe^{III}ClTPP$	−0.04
Pyridine	−0.17	H_4TPPCl_2	+0.01
$Zn^{II}TPP$	−0.18	Na_2Pc	−0.18
$Co^{II}TPP$	−0.17	H_2TPP	
$[Fe^{III}TPP]_2O$	−0.18	Aza	−0.02
$Fe^{III}ClProto$	−0.18	Pyrrole	−0.18
$Co^{II}(NO)TPP$		$Cu^{II}Pc$	−0.15
Pyrrole	−0.13	$Sn^{IV}(Pc)_2$	−0.14
NO	+0.16	H_2Pc	−0.11[a]
$Sn^{IV}Cl_2TPP$	−0.08	$Sn^{IV}F_2Pc$	−0.09
		$Fe^{II}(pip)_2TPP$	−0.13

[a] Corresponds to center of broad peak.

We see that nearly all the porphyrins of divalent ions have essentially the same charge on the pyrrole nitrogens, as do also the two compounds containing trivalent Fe, hemin Cl, and the dimeric compound $[Fe^{III}TPP]_2O$. $Co^{II}(NO)TPP$ has a pyrrole nitrogen charge which is not a great deal different from that in the compounds mentioned previously. Furthermore, all of the aforementioned binding energies of divalent and trivalent compounds are close to that of the pyrrole nitrogens of H_2TPP.

As one sees, $Fe^{III}ClTPP$ does not fit into the pattern we have outlined in the last paragraph. The nitrogen 1s binding energy in this compound is nearly 1 eV larger than that in hemin chloride. One is tempted to discard this result because it seems so anomalous, but there is no objective reason for doing so. $Fe^{III}ClTPP$ is a difficult compound to handle, but the measurements seem as reliable as those on other compounds. We have no explanation for this result and we believe it should be regarded with suspicion.

One sees, also, that the nitrogen 1s binding energy in H_4TPPCl_2, the conjugate acid of H_2TPP, is close to that of the aza nitrogens of H_2TPP.

Of the binding energies reported in Table II, those of the Fe $2p_{3/2}$ level in the trivalent and divalent Fe porphyrins are most striking. As one sees, there is a shift of 4.4 eV going from $Fe^{II}(pip)_2TPP$ to $Fe^{III}ClTPP$. In addition, the Fe $2p_{3/2}$ level in the trivalent compound is very broad, whereas that in the divalent compound is quite sharp. The Fe $2p_{3/2}$ binding energy of $Fe^{II}(pip)_2$ is parenthesized because it is uncertain. The number reported is to be viewed as an upper limit because we were not able to get an entirely satisfactory set of spectra of this compound, which is somewhat difficult to handle.

The difference in widths between the two types of compounds is probably due to unresolved multiplet splitting in the trivalent compounds, which are high spin.[17]

The difference in Fe $2p_{3/2}$ binding energies is quite large, especially by comparison with the spread of binding energies found in Fe compounds,[18] which is not large. Interpreted most simply, this would suggest that there is a difference of 0.44 e in the charge on Fe between the divalent and trivalent compounds. It is perhaps well to ask whether multiplet splitting effects might modify this. It is easy to see that this is unlikely. We may make a simplified argument, which would be correct for ionization of an s electron but which is only approximate for ionization of a p electron.[17] A core electron interacts with the d electrons by way of a coulomb interaction (C) with each d electron, minus an exchange interaction (E) with each d electron having its spin parallel to that of the core electron. So, in low spin Fe^{2+} compounds, the contribution of the d electrons to a core binding energy is $-(6C - 3E)$. In high spin Fe^{3+} there are, in our approximation, two binding energies, for core electrons antiparallel and parallel to the d electron spin. These have d-electron contributions to the binding energy of $-(5C)$ and $-(5C - 5E)$. The final states in the two cases have degeneracy 7 and 5, respectively, so the average contribution to the binding energy is $-(5C - 2.917E)$. Since the contribution of the d electrons, in the absence of multiplet effects, would be $-(5C - 2.5E)$, one sees that there is a residual shift of $0.42E$, or about 9% of the exchange splitting. This cannot be more than a few tenths of an electron volt because the total line widths, which include exchange splittings, are only about 3 eV.

The charge difference between the trivalent and divalent compounds is somewhat larger than one might have expected, since, on the whole, transition metal ions seem to show less variation in charge (or, at least, in binding energy) than one might have expected. For instance, one sees that $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ differ by only 1.3 eV in binding energy.

The calculations which have been performed, which we may test with our data, are mostly Hückel calculations. It may be argued that one should, then, use a charge binding energy correlation from Hückel calculations on other, simpler molecules. Such a correlation for nitrogen binding energies is known,[8] and yields a result rather different from the one we assume. It is found that nitrogen binding energies shift by about 2.5 eV per unit change of charge calculated by Hückel theory. We do not use this correlation because we feel that, since charge densities have a certain objective reality, we should use the correlation which seems, according to current knowledge, best to reflect this reality. If, then, Hückel calculations disagree with our results, we are justified in saying that Hückel calculations are wrong in their prediction of charges.

Since the binding energies reported in Tables I and II should correlate to net atomic charges, it is reasonable to try to relate our experimental results to the ex-

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(17) C. S. Fadley, ref 3, p 781.

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

Table IV. Net Charge Densities Calculated by Extended Hückel Model[a]

Compound[b]	Atom	Charge	Ref
Pyridine	N(aza)	−0.24	*j*
H_2P	N(aza)	−0.29	*i*
	N(pyrrole)	−0.09	
H_4P^+	N(central)	−0.06	*j*
$Mg^{II}P$	N(central)	−0.21	*e*
$V^{IV}OP$	N(central)	−0.17	*f*
$Mn^{II}P$	N(central)	−0.16	*e*
$Fe^{II}P$	N(central)	−0.17	*e*
	Fe	+0.22	
$Fe^{II}(H_2O)_2P$	N(central)	−0.195	*g*
	Fe	+0.15	
$Fe^{III}ClP$	N(central)	−0.18	*g*
	Fe	+0.26	
$Fe^{III}(CN)_2P$	N(central)	−0.15	*g*
	N(CN)	−0.21	*i*
	Fe	+0.21	
$Co^{II}P$	N(central)	−0.18	*e*
	Co	+0.34	
$Ni^{II}P$	N(central)	−0.19	*e*
	Ni	+0.30	
$Cu^{II}P$	N(central)	−0.18	*e*
	Cu	+0.28	
$Zn^{II}P$	N(central)	−0.185	*e*
	Zn	+0.40	
$Ge^{IV}(OH)_2P$	N(central)	−0.16	*h*
	Ge	+0.65	
$Sn^{IV}Cl_2P$	N(central)	−0.16	*i*
	Sn	+0.64	
Zinc chlorin	N(pyrrole)	−0.20	*i*
	N(aza)	−0.15	
	Zn	+0.40	
H_2Pc[c] (bonded)	N(aza)	−0.25	*i*
	N(pyrrole)	−0.05	
	N(bridge)	−0.20	
H_2Pc[c] (bridged)	N(center)	−0.16	*i*
	N(bridged)	−2.20	
MgPc	N(center)	−0.17	*i*
	N(bridge)	−0.20	
$Fe^{II}Pc$	N(center)	−0.12	*i*
	N(bridge)	−0.20	
	Fe	+0.25	
$Fe^{II}(pyr)_2TAP$	N(center)	−0.171 and −0.13[d]	*j*
	N(bridge)	−0.20	
	N(pyr)		
	Fe	+0.22	
$Co^{II}Pc$	N(center)	−0.15	*i*
	N(bridge)	−0.18	
	Co	+0.36	
$Ni^{II}Pc$	N(center)	−0.14	*i*
	N(bridge)	−0.18	
	Ni	+0.31	
$Ni^{II}(pyr)_2TAP$	N(center)	−0.17	*j*
	N(bridge)	−0.20	
	N(pyr)	−0.12	
	Ni	+0.34	
$Cu^{II}Pc$	N(center)	−0.15	*i*
	N(bridge)	−0.20	
	Zn	+0.33	
$Zn^{II}Pc$	N(center)	−0.15	*i*
	N(bridge)	−0.19	
	Zn	+0.45	
$Zn^{II}TAP$	N(center)	−0.16	*i*
	N(bridge)	−0.18	
	Zn	+0.45	

[a] Table prepared by Professor M. Gouterman and Dr. A. M. Schaffer at the Chemistry Department, University of Washington, Seattle. [b] Abbreviations: P (porphine); Pc (phthalocyanine); TAP (tetrazaporphine); pyr (pyridine). [c] Bonded and bridged refer to location of the central protons. See footnote *h*. [d] The densities −0.17 and −0.13 for the central N atoms differ with respect to plane set by the pyridines. The two N atoms in the plane of the pyridines are −0.13, while the two N atoms perpendicular to this plane are −0.17. [e] M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1965); **8**, 26 (1967). [f] M. Zerner and M. Gouterman, *Inorg. Chem.*, **5**, 1699 (1966); **5**, 1707 (1966). [g] M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966). [h] A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta*, **18**, 1 (1970); ref 16. [i] A. M. Schaffer, Ph.D. Thesis, Chemistry Department, University of Washington, 1972. [j] M. Gouterman and A. M. Schaffer, unpublished results.

tended Hückel calculations of Gouterman and coworkers, who have carried out the most extensive systematic studies on these systems. Some of their net atomic charges are reported in Table IV. We find a number of results from this theory that can be nicely compared with our experimental studies.

(i) The aza and pyrrole nitrogen atoms of porphine are calculated to differ by 0.2 electron. From the relation 10 eV/electron, our voltage difference in Table I implies 0.19 electron.

(ii) We find the diacid nitrogen similar to the pyrrole value, in keeping with calculations.

(iii) In the free base phthalocyanine there is calculated to be 0.18 electron difference among the three types of nitrogens for the bonded structure. This is a structure where the central protons bond to one pair of central nitrogens. For the metallophthalocyanines a considerably smaller difference is predicted for the two types of nitrogen atoms. This agrees with the broadness observed for H_2Pc. Perhaps hydrogen bonding prevents resolution of two distinct peaks in H_2Pc.

(iv) The nitrogens in the various metal salts do not differ very much from metal to metal. In view of our uncertainty in experimental values, these calculated differences may be within experimental error.

(v) For the iron atom, EH theory predicts that the ligand influences net charge comparable in amount to oxidation state. This may or may not be correct. Because of the experimental uncertainties, we cannot say for sure if this is verified by the experiments.

Conclusions

Our results from X-ray photoelectron spectroscopic studies of porphyrin and phthalocyanine compounds show, we believe, the power of the technique in answering certain questions and also provide, even in the present state of rudimentary development of the technique, unique information on the ground electronic states of these compounds. We consider our most striking results to be the demonstration of two kinds of nitrogen in porphine free base, the demonstration of the similarity of the two kinds of nitrogen in metal phthalocyanines and the suggestion that the Fe in oxidized and reduced iron porphyrins differs in charge by about 0.44 electron. The good agreement between our results and the calculations of Gouterman and coworkers gives us hope that a combination of X-ray photoelectron spectroscopy and theory will prove fruitful in attacking the structure of complex systems.

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Solvolysis of Iodopentaaquochromium(III) Ion in Acidic Aqueous Dimethyl Sulfoxide[1,2]

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Abstract: The kinetics and stereochemical course of reactions of $Cr(OH_2)_5I^{2+}$, *cis*- and *trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$, and *cis*- and *trans*-$Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$ in acidic aqueous dimethyl sulfoxide have been studied. The solvolysis of $Cr(OH_2)_5I^{2+}$ in this solvent gives *trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$ confirming a suggestion of Moore, Basolo, and Pearson. This species then loses iodide to give both isomeric species of the composition $Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$. Both isomers of $Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$ are produced when chromium(II) is oxidized with triiodide ion in acidic aqueous dimethyl sulfoxide. Identification of isomeric species was accomplished by consideration of their reactivity patterns and by comparison of their relative abundances with the statistically expected values. The earlier identification of *cis*-$Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$ as the more easily eluted bis(dimethyl sulfoxide)chromium(III) species has been confirmed.

Of the halopentaaquochromium(III) ions, that involving iodide ion as ligand is the least stable in both a thermodynamic[3] and a kinetic[4] sense. Coordinated iodide also labilizes other ligands bonded to chromium(III).[5,6] Moore, Basolo, and Pearson[5] assumed that this labilization is localized at the site trans to the bound iodide ion, but this was not proved. The situation is more complicated than implied in their paper; both isomeric tetraaquobis(dimethyl sulfoxide)chromium(III) species are produced when iodopentaaquochromium(III) ion solvolyzes in aqueous dimethyl sulfoxide.[7,8]

The present study deals with the solvolysis of iodopentaaquochromium(III) ion[9] in mixed water–dimethyl sulfoxide solvent with a mole fraction of dimethyl sulfoxide (Z) of 0.705.[10] One objective was detection of the iodo(dimethyl sulfoxide)chromium(III) ion intermediate, which would be present in the solvolysis of iodochromium(III) ion in aqueous dimethyl sulfoxide if the labilization by iodide occurs as suggested.[5] Identification of the geometry of this intermediate also was an important objective. Because of the extraordinary inertness of (dimethyl sulfoxide)chromium(III) species[7] and the separability of the isomeric species with two, three, and four molecules of dimethyl sulfoxide coordinated to chromium(III),[7] study of this system was expected to be particularly informative with respect to these objectives as well as others. Regrettably the study does not shed much additional light on the question of whether the loss of coordinated iodide by chromium(III) ion generates a pentacoordinated intermediate.[6,11]

A number of reactions interconverting species of the type $Cr(OH_2)_{6-d-i}(OS(CH_3)_2)_dI_i{}^{(3-i)+}$ have been studied in the mixed solvent in the course of this work. These reactions are indicated in Scheme I in which each species is represented by the notation (d,i). In addition the loss of iodide by cis (1,1) and trans (1,1) was studied in acidic aqueous solution.

Experimental Section

Reagents. Doubly distilled water was used in the preparation

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(1) Taken in part from the Ph.D. Thesis of Dennis B. Vanderheiden, University of Colorado, 1972.

(2) This work was supported by National Science Foundation Grant, GP 7185-X.

(3) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, 7, 1915 (1968).

(4) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

(5) P. Moore, F. Basolo, and R. Pearson, *Inorg. Chem.*, 5, 223 (1966).

(6) S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 92, 1215 (1970).

(7) L. P. Scott, T. J. Weeks, Jr., D. E. Bracken, and E. L. King, *J. Amer. Chem. Soc.*, 91, 5219 (1969).

(8) This observation was the result of a single experiment in which an aqueous solution of iodopentaaquochromium(III) ion was added to pure dimethyl sulfoxide. The solvent composition changed, therefore, as addition proceeded.

(9) Hereafter this species will be called iodochromium(III) ion. In general for chromium(III) species with coordination number six, all ligands other than water will be given in a name. For postulated unstable pentacoordinated species, all ligands including water will be specified in the name.

(10) In calculation of the composition of the mixed solvent, only the solvent components are considered.

(11) M. Ardon, *Inorg. Chem.*, 4, 372 (1965).