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Electronic Structure of Transition Metal Complexes. III. A Comparative Study of Bondings in Metal Porphyrins

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In order to elucidate π-type interaction between the metal and the ligand, the electronic structure of various metal porphyrins, [M(Por)], where M=Mn, Fe, Co, Ni, and Cu, has been investigated by the CNDO/2 method. The present calculation shows that the nature of σ-type interaction in M–N bond of porphyrin complex is similar to that of the corresponding ammine complex. The calculated ionization potentials reproduce the experimental data. The electron population of macrocycle π-electron systems in metal porphyrins is about 18 which accords with Hückel's $4n+2$ rule.

In the previous paper,[1] we discussed the mutual influence in ammine complexes of the first transition metals, in which a ligand, NH_3, coordinates to the metal with the lone pair of atom N and has no π-type MO's available. Our next interest is to consider the π-type interaction between the metal and the ligand. Probably, porphyrin is the most interesting ligand for such a purpose. Therefore, in this paper, the electronic structure of various planar metal porphyrins is investigated by the MO theory.

As well known, metal porphyrins are important in the fields of chemistry and biology. For this reason, many experimental and theoretical works have been done.[2] Several *ab initio* and semiempirical MO calculations of metal porphyrins have been carried out in order to elucidate their physicochemical properties.[3] However, most of them have been concerned with heme(Fe-porphyrin) and there are quite a few theoretical works on metal porphyrins in which central metal ions are varied widely. A systematic study of metal porphyrins has been done only with the EHMO method by Zener and Gouterman.[4]

In order to elucidate the nature of metal-ligand bond, particularly, π-type interaction, we have carried out the CNDO/2 calculations of various metal porphyrins systematically using our new bonding parameters.[5] The reason why we use the CNDO/2 method is as follows: The surprising progress in the computer as well as the development of new methods has resulted in the application of the *ab initio* MO method to medium sized molecules. It is, however, not easy to do such calculations on very large molecules, for example, metal porphyrins. In this respect, the semiempirical MO method is still useful for comparative theoretical study of similar and very large molecules.

Calculations

In this paper, metal porphyrins, [M(Por)], where M=Mn, Fe, Co, Ni, and Cu, are considered (see Fig. 1). As the bivalent ions and the porphyrin dianion are taken into consideration, the complex is neutral. Standard values have beenused for CNDO/2 parameters associated with atoms C, N, and H,[6] while a new parameter set which we proposed in the previous paper[5] has been used for those associated with the metals.

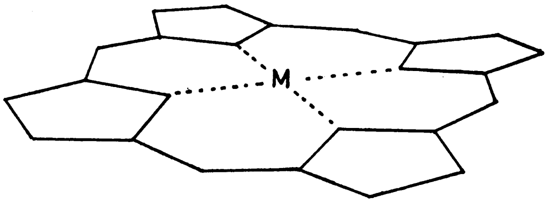

Fig. 1. Planar metal porphyrins, M(Por), where M=Mn, Fe, Co, Ni, and Cu.

Fleischer[7] and Fleischer *et al.*[7] determined molecular dimensions of various metal porphyrins by X-ray analysis. For the sake of simplicity, we assumed the D_{4h} symmetry for the porphyrin molecular framework.[8] The interatomic distances associated with M–N bonds are fixed at 2.0 Å from Mn to Cu. Furthermore, metal porphyrins are supposed to be of planar structure, because they are assumed to be in the low spin state.[9] As we make a comparative study of a series of metal porphyrins, the above-mentioned simplification on the molecular geometry is acceptable.

Results and Discussion

Binding Energy and Stability. The calculated binding energies of metal porphyrins are shown in Fig. 2. This figure shows that the order of the binding energies is as follows:

$$\mathrm{Mn} > \mathrm{Fe} > \mathrm{Co} > \mathrm{Ni} \gtrsim \mathrm{Cu},$$

and that the shape of the binding energy curve is very

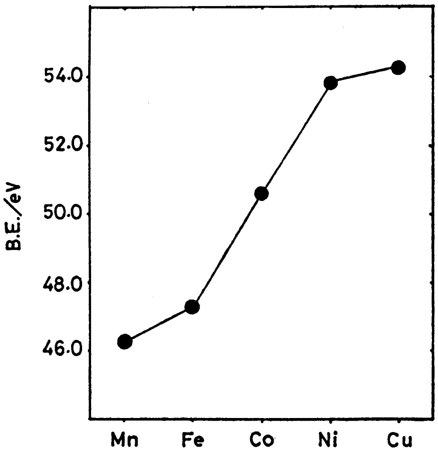

Fig. 2. Calculated binding energies (B.E.) of M(Por)'s.

similar to that of hexaammine or hexaaqua complex.[1] Unfortunately, no experimental data of the binding energies of metal porphyrins are available. However, when calculated binding energies of metal porphyrins are plotted against log (K/mol^{-3} dm^9) (K is stability constant) of the corresponding ethylenediamine complexes determined experimentally,[10] a linear relation is obtained (Fig. 3). Thus, the strength of metal-ligand bonds in metal porphyrins is parallel to that of the corresponding ethylenediamine complexes. This suggests that the strength of metal-ligand bond is determined mainly by the σ-type interaction and that the π-type interaction contributes little to it.

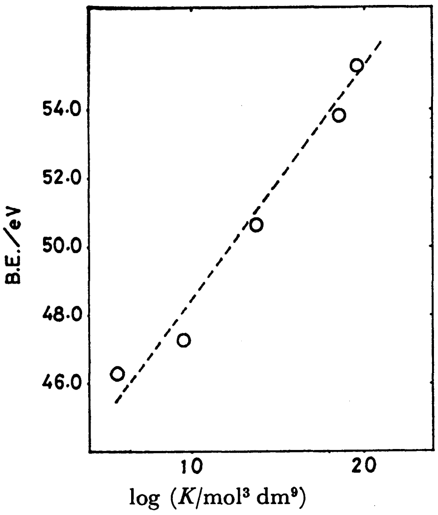

Fig. 3. Binding energy (B.E.) of M(Por) *vs.* log (K/mol^{-3} dm^9), where K is a stability constant of the corresponding ethylenediamine complex.

Bond Order and Bond Strength. As seen from Fig. 2, the calculated binding energy of Cu-porphyrin is nearly equal to that of Ni-porphyrin. This peculiar tendency has been found also with hexaammine and hexaaqua complexes.[1] In order to elucidate this problem, the strength of M–N bond is analyzed from calculated bond orders.

Bond strength is proportional to atomic bond order.[11] However, atomic bond order should not be regarded as a simple sum of bond orders associated with each orbital pair. Therefore, the relative bond strength of M–N bond is considered by comparison of bond orders associated with each orbital pair. The calculated bond orders are shown in Fig. 4. This figure shows that the change of the bond orders associated with 4s-2pσ, 4pσ-2pσ, 3dσ-2s, 3dσ-2pσ, and 3dπ-2pπ is remarkable.

The pattern of the bond-order changes in metal porphyrins is almost the same as those of hexaammine and hexaaqua complexes, as far as σ-type interaction is concerned. The bond orders associated with 3dσ-2s and 3dσ-2pσ decrease abruptly at Cu-porphyrin, as in hexaammine and hexaaqua complexes. This is due to the fact that one of the 3d electrons should enter into the antibonding orbital in the Cu complex. Thus, the decrease in the bond energy contributed from the 3dσ-2s and 3dσ-2pσ pairs cancels out the increase in that contributed from the 4s-2pσ and 4pσ-2pσ pairs. Consequently, the shape of binding energy curve shown in Fig. 2 is obtained.

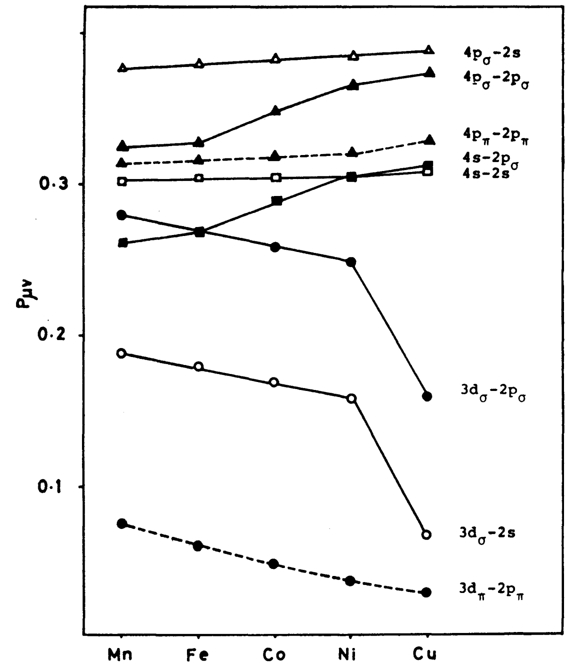

Fig. 4. Calculated bond orders associated with M–N bond in M(Por).

As we expected, the interaction of 3dπ-2pπ is small, because all the complexes are assumed to be in the low spin state in this work. The bond order associated with 3dπ-2pπ decreases according to the increase in atomic number. The reason for this is as follows: Although the ionic radii of the central metal ions decrease according to the increase in atomic number, we fixed the M–N bond distance at 2.0 Å. Therefore, the overlap integral between the metal and ligand will be caused to decrease due to the orbital contraction of the central metal ions.

It can be concluded that the nature of σ-type interaction in the M–N bonds of the porphyrin complexes is similar to that of the corresponding ammine complexes.

Orbital Energy and Ionization Potential. As we assumed these complexes to be in the low spin states, Fe- and Ni-porphyrins are in singlet states, while the others are in doublet states. Figure 5 shows orbital energies of the metal porphyrins. From this figure, some interesting results are derived.

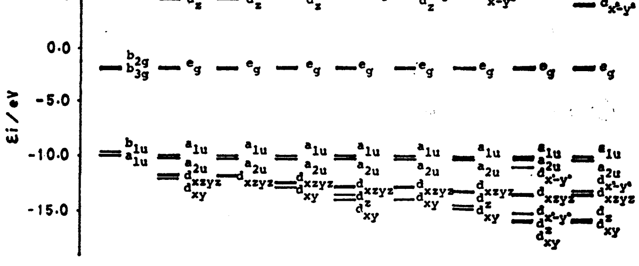

Fig. 5. MO energies (ε_i) of PH$_2$ and M(Por).

TABLE 1. SPIN DENSITIES OF M(Por)

	Mn	Co	Cu
$3d_{z^2}$	0.0	0.970	0.0
$3d_{x^2-y^2}$	0.0	0.0	0.891
$3d_{xy}$	0.986	0.0	0.0
$3d_{yz}$	0.0	0.0	0.0
$3d_{zx}$	0.0	0.0	0.0

First of all, the change in central metal ions affects MO's which are contributed mainly by the metal itself but barely affects them which are contributed by porphyrin. Although UHF calculations have been done with respect to Mn-, Co-, and Cu-porphyrins which have the open shell structure, the orbital energies of porphyrin parts associated with α- and β-spins resemble each other. In SOMO which has 3d character, the α-spin orbital is different from the β-spin orbital (*e.g.*, d_{xy}-orbital in Mn-porphyrin). This is similar to the result obtained by *ab initio* MO calculations.[12] These results may be due to the following fact that, since most of the MO's are localized on either the ligand or the central metal ion, those belonging to the latter are characterized by the metal itself. The results of calculated spin density given in Table 1 confirm this expectation. It should be noted that in Mn-porphyrin the unpaired spin has π-character, whereas it has σ-character in Co- and Cu-porphyrins. The calculated results accord with the experimental data.[2]

Secondly, although HOMO is b_{1u} (a_{2u} in D_{4h} symmetry) and NHOMO (next HOMO) is a_{1u} in PH_2 (free porphyrin), HOMO is a_{1u} and NHOMO is a_{2u} in all metal porphyrins. The a_{2u} goes down due to $4p\pi$-$2p\pi$ interaction. Figure 6 shows the orbital interaction diagram. This figure indicates that the $4p\pi$-orbital of the metal ion interacts with the a_{2u} of Por^{2-} (porphyrin dianion) but not with the a_{1u} because of its nonbonding character. Therefore, the a_{1u} energy of PH_2 is almost the same as that of metal porphyrin. Table 2 gives calculated ionization potentials which are obtained by using Koopmans' theorem together with experimental data.[13] As shown from this table, the calculated results reproduce the experimental data, that is, the order of the a_{1u} and a_{2u} is reversed when PH_2 coordinates to the metal. Thus, the present results also suggest that the bonding parameter, $\beta_\mu{}^0(4p)$, is reasonable. Furthermore, the experiment using ESCA shows that the MO energy of PH_2 is almost the same as that of metal porphyrin. The present calculation also explains this fact. Accordingly, it is suggested that Por^{2-} becomes neutral by coordinating to a bivalent metal. This is different from the results calculated by the *ab initio* MO method which are shown in Table 2 for comparison.

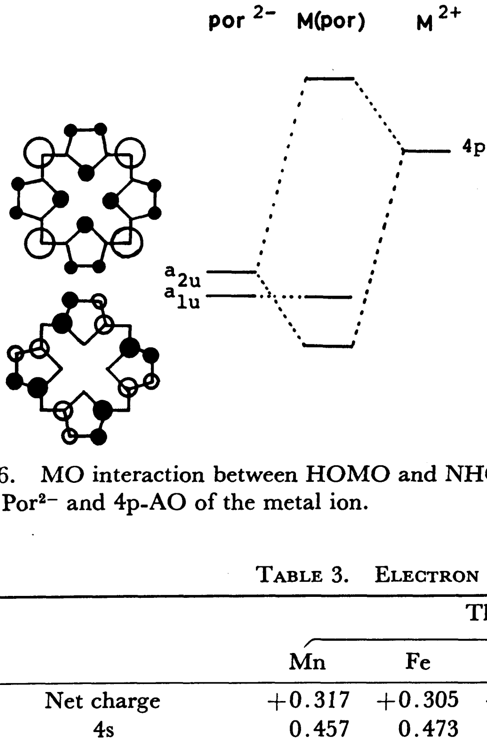

Fig. 6. MO interaction between HOMO and NHOMO of Por^{2-} and 4p-AO of the metal ion.

TABLE 2. IONIZATION POTENTIALS, I_p, OF PH_2 AND M(Por)

		I_p/eV			
		PH_2	Fe	Co	Ni
This calcd	a_{1u}	8.82	8.88	8.88	8.88
	a_{2u}	8.57	9.03	9.07	9.10
Ab initio[a]	a_{1u}	8.78		6.82	
	a_{2u}	8.42		7.12	
Obsd[b]	a_{1u}	6.72	6.50		6.44
	a_{2u}	6.39	6.80		6.62

a) Ref. 12. b) Ref. 13.

Electronic Spectra. The lowest electronic transitions are contributed mainly by the HOMO and LUMO of the complex. In the present study, we obtained the result that the HOMO and LUMO of the complex are localized entirely in the porphyrin part and that their character is very similar among complexes. Therefore, the variation in transition energy is proportional to that in the orbital energy difference between the HOMO and LUMO.

Figure 5 shows that both HOMO and LUMO are almost unchanged by the replacement of metal ions, so that the difference between them is nearly constant. This fact consists with the results obtained through measurement of electronic spectra in which absorption maxima of metal porphyrins are almost the same.[14]

Electronic Population and Net Charge. Let us consider charge densities. Figure 7 shows the calculated

TABLE 3. ELECTRON POPULATION ON THE METAL ION OF M(Por)

	This calcd					EHMO[a]	*Ab initio*[b]
	Mn	Fe	Co	Ni	Cu	Co	Co
Net charge	+0.317	+0.305	+0.260	+0.223	+0.258	+0.342	+1.78
4s	0.457	0.473	0.523	0.563	0.576	0.442	0.11
4p	0.940	0.966	1.003	1.040	1.084	0.599	0.13
3d	5.285	6.258	7.214	8.174	9.083	7.637	6.98

a) Ref. 4. b) Ref. 12.

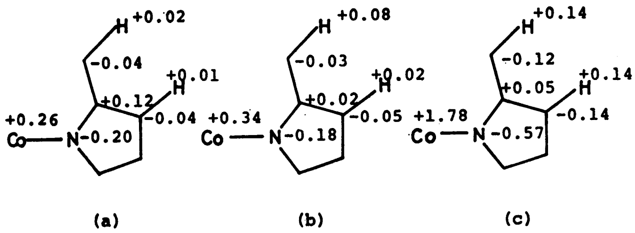

Fig. 7. Calculated net charges of Co-porphyrin.
(a): This calcd, (b): EHMO method, Ref. 4, (c): *ab initio* MO method Ref. 12.

net charge of Co-porphyrin. For comparion, the results obtained by the EHMO and *ab initio* MO methods are also shown. Although the values of calculated net charges depend greatly on the method used, the aspects of polarization resemble each other. The calculated net charge based on the CNDO/2 or EHMO method shows that the central metal ion is almost neutral. This result is different from that calculated by the *ab initio* MO method. For comparison, the calculated charge densities of the central metal ion are shown in Table 3. From this table, it is seen that both the CNDO/2 and EHMO methods calculate the large electron population in the 4s- and 4p-AO's. This is the reason why the central metal ion is neutralized by the coordination. In the EHMO method, the value of q(3d) is also large. Our results coincide with recent X-ray data in which the valence electron distribution is analyzed in detail[15] and also with the results of ionization potential obtained from the photoelectron spectra mentioned above.

In free porphyrin, its macrocycle is highly conjugated and a number of resonance forms can be written. There are nominally 22 π-electrons, but only 18 of them are included in any one delocalization pathway.[2] In metal porphyrin, the very large stability of the porphyrin part may be due to the high aromaticity of the macrocycle part, which is expected to have 18 π-electrons (Hückel's $4n+2$ rule). In order to confirm this, the calculated π-electron density of the macrocycle part is given in Table 4, together with the result calculated by the P-P-P method.[8] This table shows that the number of π-electrons in macrocycle is nearly equal to 18 as expected.

TABLE 4. CHARGE DENSITIES OF MACROCYCLE PART OF M(Por) AND Por^{2-}

	This calcd						P-P-P[a] M(Por)
	Por^{2-}	Mn	Fe	Co	Ni	Cu	
Q	17.49	17.58	17.57	17.57	17.56	17.54	17.75

a) Ref. 8.

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