Inorganica Chimica Acta, 58 (1981) 107–112
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Electronic Structure of Porphyrins.
II. Mutual Influence between Ligands of Co(III)–Porphyrins

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Received July 6, 1981

CNDO/2 calculations of hexacoordinate Co(III)–porphyrins, [Co(III)(Por)XY] and hexacoordinate tetraammine Co(III) complexes, [Co(III)(NH$_3$)$_4$XY], where X = CO and CN$^-$ and Y = CO, Im, Py and NH$_3$ have been carried out. As the energy differences between HOMO and LUMO are almost constant for all hexacoordinate Co(III)–porphyrins, their electronic spectra associated with the lowest electronic transitions are similar to each other. In hexacoordinate metal porphyrins, there seems to occur charge breathing between the axial ligand and the H's in porphyrin. The strength of the metal–porphyrin bond is larger than that of the metal–NH$_3$ bond. This brings the bond weakening of M–X bond in metal porphyrins in comparison with tetraammine complexes, which seems to be responsible for the interesting catalytic ability of metal porphyrins. The effect of the fifth ligand is almost absorbed by the 4pπ–2pπ interaction between the metal and porphyrin.

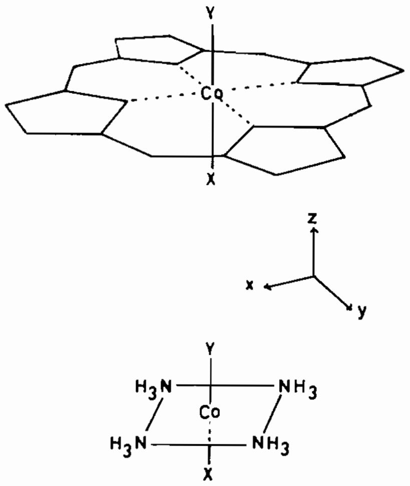

Fig. 1. Hexacoordinate Co(III)–porphyrins, [Co(III)(Por)XY], and hexacoordinate tetraammine Co(III) complexes, [Co(III)(NH$_3$)$_4$XY], where X = CO and CN$^-$ and Y = CO, Im, Py and NH$_3$.

Introduction

In the previous paper [1] we studied the nature of the electronic spectra of porphyrins using a modified MN expression for the two-electron repulsion integral which takes partly into account the effect of the electronic correlation by Brueckner–Goldstone scheme [2]. Many theoretical studies of electronic spectra of porphyrins have been done [3]. However, all of these works calculated the N band away from the Soret band. Our calculation gave the N band at almost the same region as the Soret band which agreed with the experimental data [4].

In this paper we will investigate theoretically the mutual influence between the ligands of metal porphyrins. Recently, we proposed a new CNDO/2 parameter set for the first transition metals [5]. Our parameter gives reasonable values of the binding energy of the metal–ligand bond, and also explains the mutual influence between the ligands of various pentaammine complexes [6]. The mutual influence between the axial ligands of metal porphyrins has received much attention from chemists and biologists for the last few decades, particularly with respect to the oxygen binding and releasing in heme (Fe(II) protoporhyrin IX). Heme has some interesting properties, such as the allosteric effect in the oxygen binding and electron transfer in biological oxidation–reduction systems. Thus, heme plays a very important role as a catalyst in biological systems. Catalysts should have the following properties: the binding between the catalyst and substrate should not be too weak and should not be too strong, because in the former case the catalyst does not catch the substrate and in the latter case it produces a compound. In this respect, the porphyrin part of metal porphyrin plays a key role for the control of strength of the binding between the metal and substrate. In order to make clear this problem, we will also calculate hexacoordinate tetraammine complexes and compare the calculated results with those of metal porphyrins.

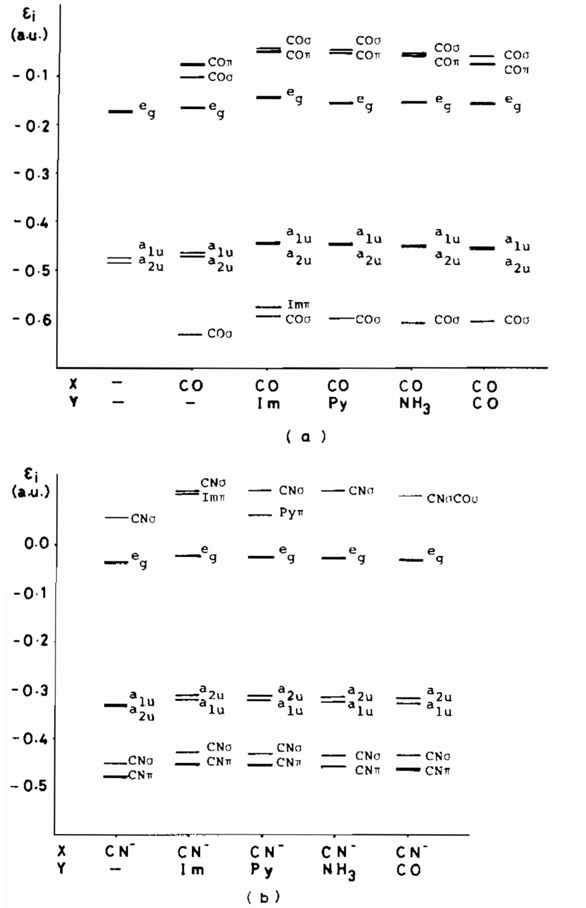

Fig. 2. Calculated MO energies of [Co(III)(Por)] and [Co(III)(Por)XY]. (a) X = CO; (b) X = CN$^-$.

The reason why we use the CNDO/2 method is as follows: The surprising progress in the use of computers, as well as the development of new methods, has resulted in the application of *ab initio* MO method to molecules of medium size. It is, however, not easy to do such calculations of very large molecules, such as metal porphyrins. In this respect, the semi-empirical MO method is still useful for the comparative theoretical study of similar and very large molecules.

Calculations

CNDO/2 calculations of hexacoordinate Co(III)–porphyrins, [Co(III)(Por)XY] and hexacoordinate tetraammine Co complexes, [Co(III)$(NH_3)_4$XY], where X = CO and CN$^-$ and Y = CO, Im(Imidazole), Py(Pyridine) and NH_3 have been carried out (Fig. 1). Standard values have been used for CNDO/2 parameters associated with the C, N, O and H atoms [7], while a new parameter set [5] has been used for Co atom. For simplicity, the interatomic distance associated with Co(III) and coordinating atom of the ligand is fixed at 2.0 Å. We assumed the same geometry for the porphyrin molecular framework as that given in the previous paper [1]. For the geometry of the ligand, X or Y, we have employed the experimental data of the corresponding free molecule [8]. As we make a comparative study of the mutual influence of a series of hexacoordinate Co(III)–porphyrins, the above mentioned simplification on the molecular geometry should be acceptable.

The complexes are assumed to be in the low spin states. Accordingly, the ground state is in the singlet state.

Results and Discussion

Orbital Energy and Electronic Spectra

The role of the fifth ligand, histidine, has called particular attention to the study of catalytic ability of heme. Therefore, we chose Im, Py, NH_3 and CO as the fifth ligand, and CO and CN$^-$ as the sixth ligand. Although the oxygen is the most interesting sixth ligand, we chose not to use it because the oxygen coordinate metal porphyrins usually take the various spin states. The calculated orbital energies are shown in Figs. 2(a) and (b). These figures show some interesting results. Namely, in CO coordinate Co(III)–porphyrins (Fig. 2(a)), the a_{1u} and a_{2u} are almost degenerate, while in CN$^-$ coordinate Co(III)–porphyrins (Fig. 2(b)), the order of the a_{1u} and a_{2u} is reversed compared with that of the planar Co(III)–porphyrin. The reason for this energy reversal is due to the fact that the a_{2u} of porphyrin and that of CN$^-$ are closely located to each other. The energy differences between HOMO and LUMO are almost constant for all Co(III)–porphyrins. As the off-diagonal matrix elements of SECI (singly excited configuration interaction) matrix are almost the same for analogous compounds, we expect that the electronic spectra associated with the lowest electronic transition of Co(III)–porphyrins are similar to each other.

Trans Influence on Charge Density of the Sixth Ligand

The change of the charge density on the sixth ligand measures the magnitude of the charge transfer interaction between X and Co(III) ion. It is interesting to examine the effects of the fifth ligand and porphyrin on the change of the charge density of the sixth ligand. In order to make clear this problem, we compare the calculated results with those of the corresponding tetraammine complexes. In Figs. 3(a) and (b), the change of the total electron population of X($\Delta Q_X = Q_X - 10$) upon coordination is shown. This figure shows that ΔQ_X is almost unchanged even if the fifth ligand Y is varied. As we showed

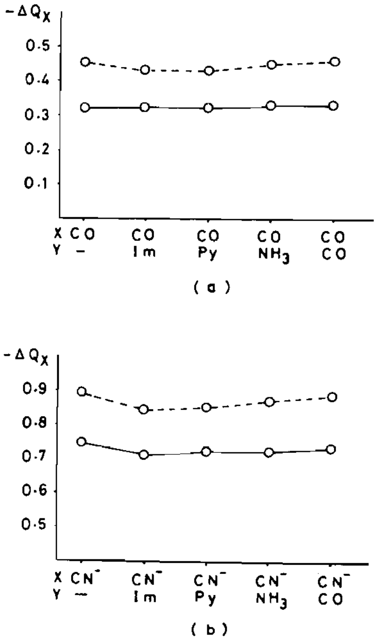

Fig. 3. Change of the total electron population of the ligand, X(ΔQ_X), in the complex; ——— [Co(III)(Por)XY], ------- [Co(III)(NH_3)$_4$XY]. (a) X = CO; (B) X = CN^-.

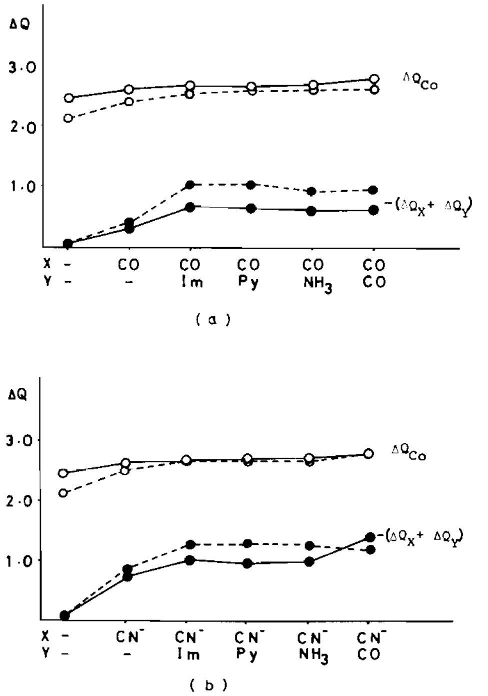

Fig. 4. Changes of the total electron populations of Co(ΔQ_{Co}) and the axial ligands X and Y(ΔQ_X + ΔQ_Y), in the complex; ——— [Co(III)(Por)XY], ------ [Co(III)-(NH_3)$_4$XY]. (a) X = CO; (b) X = CN^-.

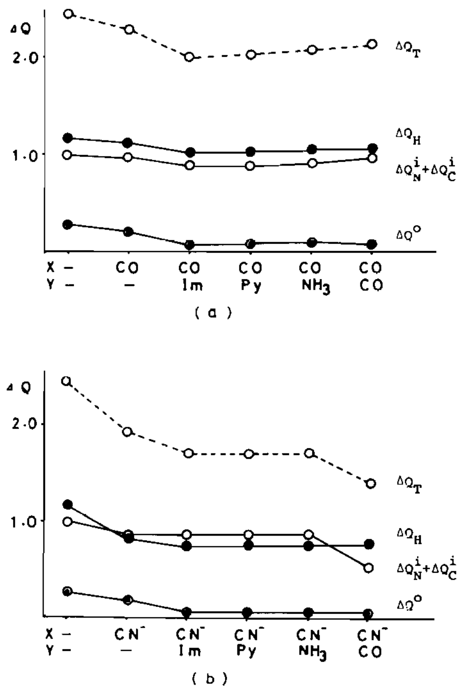

Fig. 5. Change of the total electron population of porphyrin part. (a) X = CO; (b) X = CN^-.

in the previous paper [6], the *trans* influence of the ligand in pentaammine complex in the low spin state is much smaller than that in the high spin state. Therefore, it is expected that high spin–low spin states conversion is very important for the oxygen binding and releasing in heme.

We plot the change of the electron population in the axial region X-Co(III)–Y of [Co(III)(Por)XY] and [Co(III)(NH_3)$_4$XY] in Figs. 4(a) and (b) in order to make clear the role of porphyrin. In these figures, we plot a sum of ΔQ_X and ΔQ_Y instead of individual population changes. These figures show the value of ΔQ_{Co} is nearly equal to 3, that is, Co(III) ion is almost neutralized which accords with Pauling's electron neutrality principle. On the contrary, ΔQ_X + ΔQ_Y is considerably changed. This means that the equatorial ligand, porphyrin or (NH_3)$_4$, absorbs or releases the excess charge. The magnitude of ΔQ_X + ΔQ_Y in the porphyrin complex is much smaller than that of the corresponding tetraammine complex, because the bonding between Co(III) and porphyrin is much stronger than that between Co(III) and NH_3. Accordingly, the bonding between the ligand X and Co(III) in the former is relatively weak. This will be shown in detail in the next section.

It will be interesting to analyze the change of the charge densities of porphyrin part in detail. The interaction between the metal and the equatorial ligand can be classified into two types, in and out of molecular plane-types (i- and o-parts). Thus, in Figs. 5(a) and

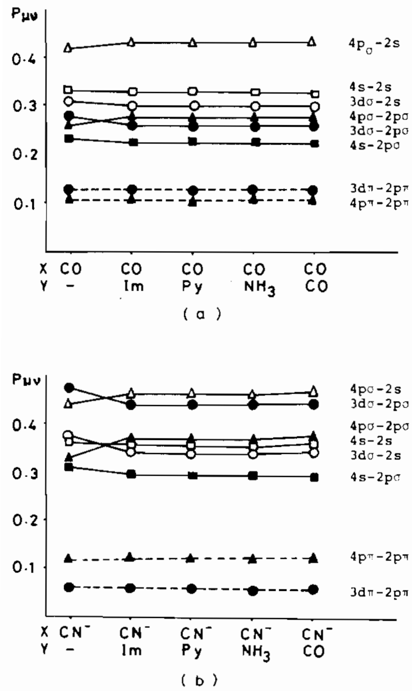

Fig. 6. Calculated bond orders associated with Co–X bond in [Co(III)(Por)XY]. (a) X = CO; (b) X = CN$^-$.

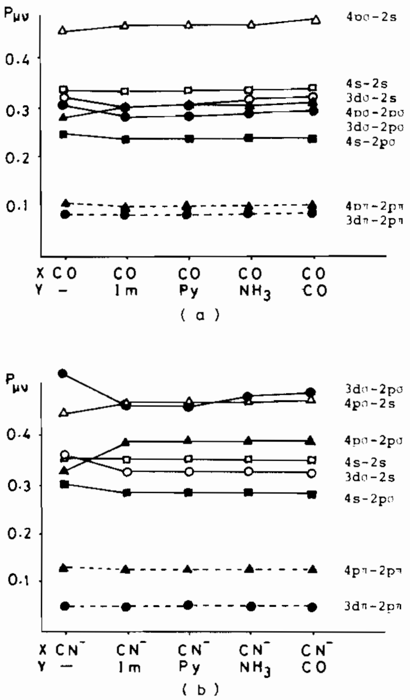

Fig. 7. Calculated bond orders associated with Co–X bond in [Co(III)(NH$_3$)$_4$XY]. (a) X = CO; (b) X = CN$^-$.

(b) the change of total electron population (ΔQ_T) of porphyrin part can be divided into i- and o-parts (ΔQ^i and ΔQ^o). Furthermore, the former consists of the contributions from coordinated N's (ΔQ^i_N), conjugated C's(ΔQ^i_C) and outer H's(ΔQ_H), respectively.

$$\Delta Q_T = \Delta Q^i + \Delta Q^o \tag{1}$$

$$\Delta Q^i = \Delta Q^i_N + \Delta Q^i_C + \Delta Q_H \tag{2}$$

These figures show that the ΔQ_T decreases with increasing coordination number (no XY, with X and with XY). This is due to the fact that when the charge migrates from the fifth and sixth ligands to Co(III) ion, it flows out into the porphyrin part. It should be noted that ΔQ_H is considerably large. Thus, the larger amount of the charge from the axial ligands flows out finally into H's, that is, this seems to look like the charge breathing between the axial ligands and H's. Such charge breathing takes place through the interaction between $d_{x^2-y^2}$ of Co(III) and 2pσ of coordinating N of porphyrin.

Bond Order and Bond Strength

Experimentally, the *trans* influence in hexacoordinate metal complexes has been observed as the change of the bond distance. For example, in heme, the *trans* influence is to be considered as the effect of the fifth ligand on the binding of substrate at the sixth position from the point of view of catalysis. Therefore, the change of the bond strength associated with the metal ion and the sixth ligand X is most interesting.

The bond strength is porportional to the atomic bond order [9]. However, the atomic bond order should not be regarded as the simple sum of the bond order associated with each orbital pair. Therefore, the relative bond strength of Co–X or Co–*cis*N bond is considered by the comparison of the bond order associated with each orbital pair.

In a metal complex, we must notice the following rather peculiar interaction between the metal and ligand. To a first approximation we can neglect the contribution of the metal dπ-orbital to the metal–ligand bond formation, because the overlap integral of 3dπ–2pπ is very small. In this respect, 4p's have a key role for mutual influence on the bond strength between the metal and ligand. $4p_z$ interacts with porphyrin π-MO's, but this orbital behaves as σ-orbital for the interaction between the axial ligand and metal. On the other hand, $4p_x$ and $4p_y$ act as σ-orbital with porphyrin and π-orbital with the axial ligand. The bond order associated with each orbital pair is shown in Figs. 6 and 7. These figures show that the bond orders associated with 3dπ–2pπ, 4pπ–2pπ, 4s–2s and 4s–2pσ of M–X bond are almost unchanged, so that other orbital pairs contribute to the mutual influence of the ligands. When the complex has the fifth ligand Y the M–X bond is

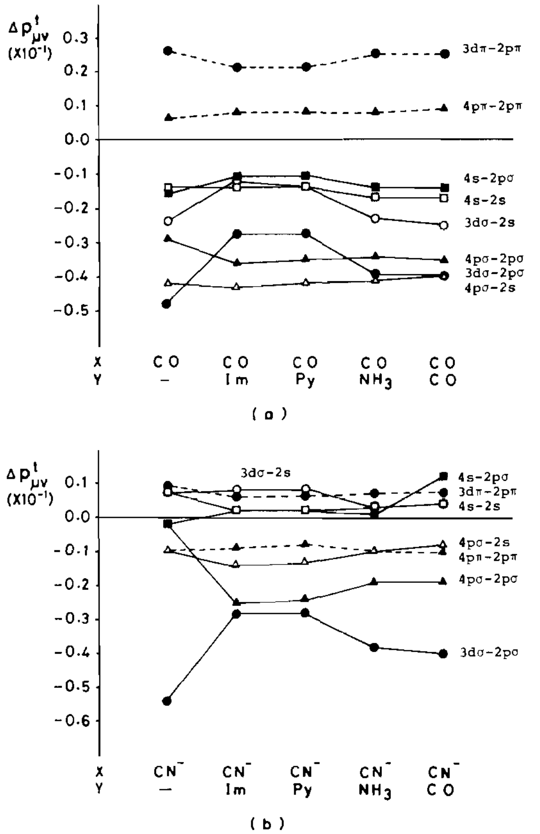

Fig. 8. Bond order difference associated with Co–X bond calculated by eqn. (3). (a) X = CO; (b) X = CN$^-$.

strengthened by the contribution of orbital pairs 4pσ–2s and 4pσ–2pσ, and weakened by 3dσ–2s and 3dσ–2pσ pairs. Namely, the 3dσ weakens the M–X bond but 4pσ strengthens it. In total, the M–X bond is slightly weakened.

It is also interesting to see the relative variation of the bond orders. In order to make clear the effect of *cis* ligand Por or $(NH_3)_4$ on the axial bond strength we plot in Fig. 8 the bond order difference associated with M–X bond,

$$\Delta p^t_{\mu\nu} = p_{\mu\nu}(\text{M–X in [Co(Por)XY]}) - p_{\mu\nu}(\text{M–X in [Co(NH}_3)_4\text{XY]}) \qquad (3)$$

This figure clearly shows that M–X bond of porphyrin complex is weaker than that of tetraammine complex. This is important for the catalytic ability of porphyrin complexes, because the binding between the metal and ligand X in the porphyrin complex is not as strong as that of the tetraammine complex or usual transition metal complexes. From this figure, we obtain the following interesting results: When we compare the bond order variation ($\Delta p^t_{\mu\nu}$) of a given orbital pair in Fig. 8(a) with the correspond-

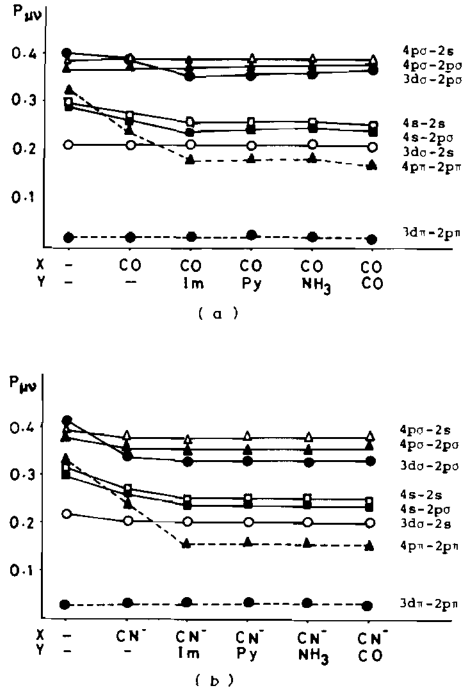

Fig. 9. Calculated bond orders associated with Co–*cis*N bond in [Co(III)(Por)XY]. (a) X = CO; (b) X = CN$^-$.

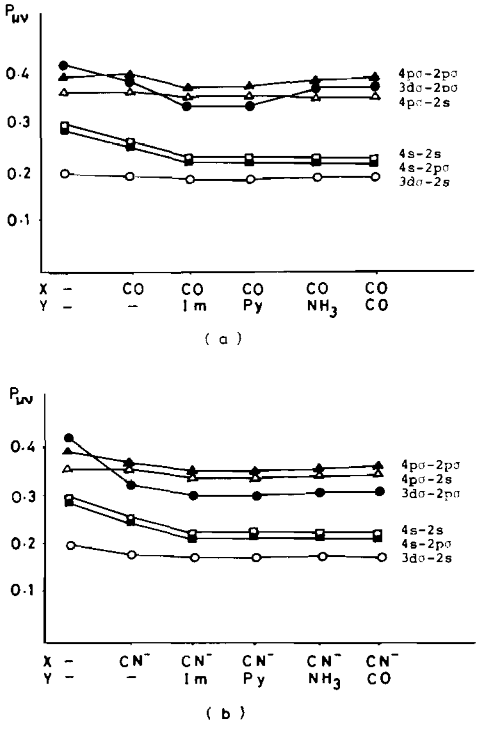

Fig. 10. Calculated bond orders associated with Co–*cis*N bond in [Co(III)$(NH_3)_4$XY]. (a) X = CO; (b) X = CN$^-$.

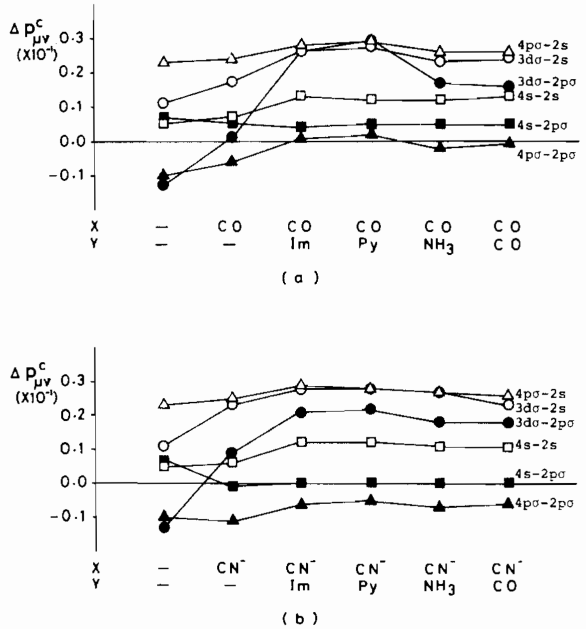

Fig. 11. Bond order difference associated with Co–*cis*N bond calculated by eqn. (4). (a) X = CO; (b) X = CN⁻.

ing one in Fig. 8(b), the characteristic features of the variations are similar to each other except for the absolute values. When tetraamine complex has Im or Py as the ligand Y the bond strength of M–X bond is weakened mainly by 3dσ–2pσ interaction, and not too much in the case of the ligand Y = NH_3 or CO.

In Figs. 9 and 10 the bond order variation of each orbital pair associated with M–*cis*N bond is shown. It is surprising that when the complex has a ligand Y the bond order variation of M–*cis*N bond is much greater than that of M–X bond. Therefore, we can say that bond weakening effect of the ligand Y is mainly absorbed at the *cis* ligand. We plot in Fig. 11 the bond order difference of M–*cis*N bond,

$$\Delta p^{c}_{\mu\nu} = p_{\mu\nu}(\text{M–}cis\text{N in [Co(Por)XY]}) - \\ - p_{\mu\nu}(\text{M–}cis\text{ N in [Co(NH}_3)_4\text{XY]}) \qquad (4)$$

This figure shows that in porphyrin complex the bond weakening power of the ligand Y is largely absorbed by the 4pπ–π* interaction between the metal and porphyrin, whereas in tetraammine complex it is absorbed by 4s–2s, 4s–2pσ and 3dσ–2pσ interactions.

In conclusion, the aspects of the mutual influence of the ligand in metal porphyrins may be summarized as follows:

1. As the energy differences between HOMO and LUMO are almost constant for all hexacoordinate Co(III)–porphyrins, their electronic spectra associated with the lowest electronic transitions are similar to each other.
2. In hexacoordinate metal porphyrins, there seems to occur charge breathing between the axial ligand and H's in porphyrin.
3. The strength of metal–porphyrin bond is larger than that of metal–NH_3 bond. This brings the bond weakening of M–X bond in metal porphyrin in comparison with the corresponding tetraammine complex. This fact seems to be responsible for the interesting catalytic ability of metal porphyrins.
4. The charge transfer interaction between the metal and the fifth ligand is almost absorbed by the 4pπ–2pπ interaction between the metal and porphyrin.

Acknowledgements

The authors would like to express their gratitude to the Computer Center of Institute for Molecular Science for the use of the HITAC M-200H computer and the Data Processing Center of Kyoto University for the use of the FACOM M-200 Computer.

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