Theoretical Study of Global and Local Charge Transfer Descriptors Applied to the Interaction of Cobalt Phthalocyanine with 2-Mercaptoethanol and Cobalt Phthalocyanine with Pyridine in the Gas Phase

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In this article, we present a theoretical study of global and local charge transfer (CT) descriptors applied to a redox reaction and to a formation reaction, i.e., the interaction between cobalt phthalocyanine and 2-mercaptoethanol and the interaction between cobalt phthalocyanine and pyridine, respectively. Global and local properties profiles were built up along a reaction coordinate defined between the atoms directly involved in each reaction. Two regions along the reaction coordinate were found for the redox reaction rationalized in terms of different kind of interactions, i.e., the *net* CT and no-interaction regions. However, the formation reaction only shows one region along the reaction coordinate, i.e., the formation region. We also found that local properties such as spin density and atomic net charge are good charge transfer descriptors because they show clearly the difference between a *net* CT and a *partial* CT along the reaction coordinate.

Introduction

Electron-transfer reactions range from very simple to very complex. In the simplest case, one electron is transferred in a so-called self-exchange reaction between two ions having the same constitution but differing by one unit in their oxidation states. There is no net chemical change in the system. In contrast, there exist other reactions very complex and involves several electron-transfer steps.[1] In the last years, the study of transition metal phthalocyanine systems as potential catalysts in redox processes has become a very important research area.[2−7] It has been shown that cobalt(II) tetrasulfophthalocyanine (Co(II)-TSPc) is a catalyst for the oxidation of 2-mercaptoethanol (2ME) in the presence of oxygen leading to disulfide species.[7] In this process, one electron is transferred from 2-mercaptoethanol anion to Co(II)TSPc leading to 2-mercaptoethanol radical and Co(I)TSPc; the former reacts with another radical forming the disulfide species, and the latter reacts with oxygen regenerating the Co(II)TSPc species. In particular, the oxidation reaction of 2-mercaptoethanol by means of cobalt(II) phthalocyanine deposited on graphite electrode has been extensively studied by Zagal's group.[8−14] Recently, we published a first theoretical study of the interaction between cobalt (II) phthalocyanine (CoPc) and 2-mercaptoethanol with and without a graphite cluster.[15] This study was performed in order to describe the interactions at a molecular level of the catalyst (CoPc) and the electrode (graphite cluster) toward the redox active substrate (2ME).[15] Quantum chemists have now considered gas phase electron transfer reactions in detail using a variety of computational methods. Not surprisingly, many of the theoretical principles that apply in the gas phase also find use in the solution models, but the complexity of the liquid environment necessarily leads to much less detailed quantum mechanical treatments that can be accorded reactions involving only a few nuclei.[16] Although experimental studies published in the literature about redox processes have been carried out in a homogeneous solution phase or heterogeneous phase, we found it interesting to describe these systems in the gas phase as a starting point for the modeling of more complicated systems, i.e., including solvent.

Quantum chemistry techniques applied to chemical systems containing transition metal atoms constitute a major challenge mainly because of their large size, and consequently, a theoretical modeling is not easy to carry out.[17] Semiempirical quantum methods are much faster than ab initio methods, and they are a good alternative for studying relatively large molecules. PM3-(tm) semiempirical model, which is an extension of the standard PM3 method for transition metal elements, has proven to be quite successful for the calculation of equilibrium geometry, including the geometry of inorganic and organometallic transition metal compounds.[16−18] Cundari et al. reported a successful prediction of geometries with the PM3(tm) method for vanadium complexes and a set of more than one hundred compounds involving all transition metals for which the parameters are available in PM3(tm) as included in the Spartan package.[17,21] Cruz et al.[22] used this method to study the polymerization ethylene catalyzed by zirconocene derivatives. These authors found a good agreement in both, geometry and energy of the different species, compared with the previously published work using ab initio methods, and Dobrowolski et al.[23] compared the PM3(tm) method with DFT and RHF in the study of dioxygen complexes and also found good agreement.

In this paper, our aim is to find charge-transfer descriptors that allow us to differentiate between a partial charge transfer (bond formation) and a net charge transfer (redox process). To study the *net* CT, we chose a redox reaction such as the oxidation of 2-mercaptoethanol by a cobalt(II) phthalocyanine. It is our interest to study the first electron transfer, i.e., electron transfer from 2-ME anion to Co(II)Pc system. On the other hand, it is well-known that pyridine is a very good ligand for the coordination of transition metal complexes. We decide to show

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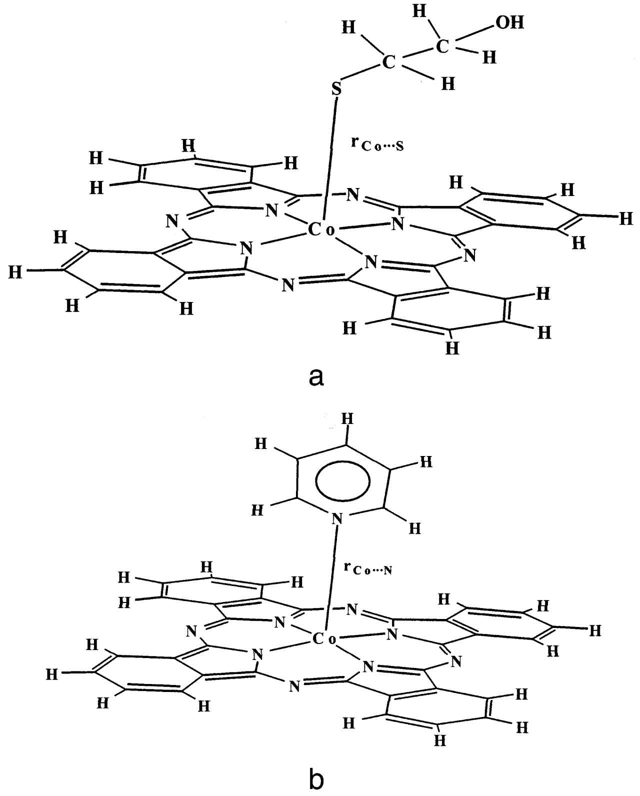

Figure 1. Structural view of the the (a) CoPc···2ME and (b) CoPc···Py systems indicating the reaction coordinate used.

the reaction coordinate for the formation reaction between Co(II)Pc and pyridine leading to the five coordinated cobalt complex as an example of *partial* CT. Profiles of different global and local properties along a reaction coordinate through which the charge transfer occurs were determined. From a global viewpoint, we studied the interaction energy and dipole moment descriptors. From a local viewpoint, the descriptors used were the spin density, atomic net charge, and Fukui function. This paper shows how a charge-transfer process can be rationalized at a theoretical level and therefore constitutes an important starting point for the study of chemical reactions which involve a redox process.

Theoretical and Computational Details

To study the redox and the formation reaction, SCF/MO semiempirical theoretical calculations using an UHF procedure were carried out for the CoPc···2ME and CoPc···Py systems along a reaction coordinate (see Figure 1). A PM3 Hamiltonian parametrized for transition metals provided by the TITAN package named PM3(tm) was used.[24] Profiles of global and local properties were constructed along two reaction coordinates. One of them was defined as the distance between the cobalt atom and the sulfur atom ($r_{\mathrm{Co\cdots S}}$) of the CoPc···2ME system for studying the reaction coordinate of the redox process. The other was defined as the distance between the cobalt atom and the nitrogen atom ($r_{\mathrm{Co\cdots N}}$) of the CoPc···Py system and was used to study the formation reaction. Full geometry optimization was performed for each distance value of the reaction coordinate in the CoPc···2ME and CoPc···Py systems; that is, we optimized the molecular geometry for the whole structure keeping a constraint in the distance between the cobalt atom and the donor atom of the substrate (S, 2ME; N, Py).

For the CoPc···Py system, a set of distance values for the reaction coordinate ranging from 5.2 to 1.4 Å region was chosen. For the CoPc···2ME system, the distance values for the reaction coordinate that were varied from 5.2 to 3.8 Å were chosen. In the case of the CoPc···2ME system, the anion derived from 2-mercaptoethanol was used, and therefore, the total charge of the complete system is -1, and the multiplicity is a doublet due to the unpaired electron of the Co(II) species. For the CoPc···Py system, a total charge equal to zero and a multiplicity of doublet was used.

The studied global properties along $r_{\mathrm{Co\cdots S}}$ and $r_{\mathrm{Co\cdots N}}$ correspond to the dipole moment and the interaction energy obtained directly from the theoretical calculations. The latter is defined for the redox reaction as

$$E_{\mathrm{int}}(r_{\mathrm{Co\cdots S}}) = E_{\mathrm{system}}(r_{\mathrm{Co\cdots S}}) - (E_{\mathrm{CoPc}} + E_{\mathrm{2ME}}) \tag{1}$$

and for the formation reaction as

$$E_{\mathrm{int}}(r_{\mathrm{Co\cdots N}}) = E_{\mathrm{system}}(r_{\mathrm{Co\cdots N}}) - (E_{\mathrm{CoPc}} + E_{\mathrm{Py}}) \tag{2}$$

On the other hand, the local properties studied in this paper along $r_{\mathrm{Co\cdots S}}$ and $r_{\mathrm{Co\cdots N}}$ correspond to (a) spin density of the atoms involved directly in the charge transfer, that is the pair (Co,S) for the CoPc···2ME system and the pair (Co,N) for the CoPc···Py system; (b) atomic net charge of the same atoms mentioned above, that is the pair (Co,S) and the pair (Co,N) by using the Natural Atomic Orbital (NAO) approximation; and (c) Fukui function $f^{-}(\vec{r})$ defined for an electrophilic attack.

The Fukui function was proposed in the literature as a tool for deducing the relative reactivity of different positions in a molecule by Parr and Yang[25] and provides information about the reactivity of the most probable site where the reaction would occur. Fukui function is defined as

$$f(\vec{r}) = \left(\frac{\delta\mu}{\delta\nu(\vec{r})}\right)_N = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{\vec{\nu}} \tag{3}$$

where μ is the electronic chemical potential, ν is the external potential, ρ corresponds to the electronic density, and N is the total number of electrons of the system. The second member of eq 3, written as $[\partial\rho(\vec{r})/\partial N]_{\vec{\nu}}$, shows that it is a quantity involving the electron density of the atom or molecule in its frontier, i.e., the valence region. The Fukui function shows the site of highest reactivity, because it gives the largest variation of the electronic density for a molecular system when it accepts or donates electrons. Then, we may assume that the preferred site is the one with the largest value of $f(\vec{r})$ in the system, that is where the largest variation of $\rho(\vec{r})$ with respect to N would occur. Equation 3 as such provides three reaction indexes because $\rho(\vec{r})$, as a function of N, has discontinuities.[23] Therefore, one can define three different types of Fukui function:

$$f^{+}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{+\nu(\vec{r})} = [\rho_{N+1}(\vec{r}) - \rho_{N}(\vec{r})] \approx \rho_{\mathrm{LUMO}}(\vec{r}) \tag{4}$$

governing nucleophilic attack

$$f^{-}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{-\nu(\vec{r})} = [\rho_{N}(\vec{r}) - \rho_{N-1}(\vec{r})] \approx \rho_{\mathrm{HOMO}}(\vec{r}) \tag{5}$$

governing electrophilic attack

$$f^{0}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{0\nu(\vec{r})} = \frac{1}{2}[f^{+}(\vec{r}) + f^{-}(\vec{r})] \approx \frac{1}{2}[\rho_{LUMO}(\vec{r}) + \rho_{HOMO}(\vec{r})] \tag{6}$$

governing radical attack.

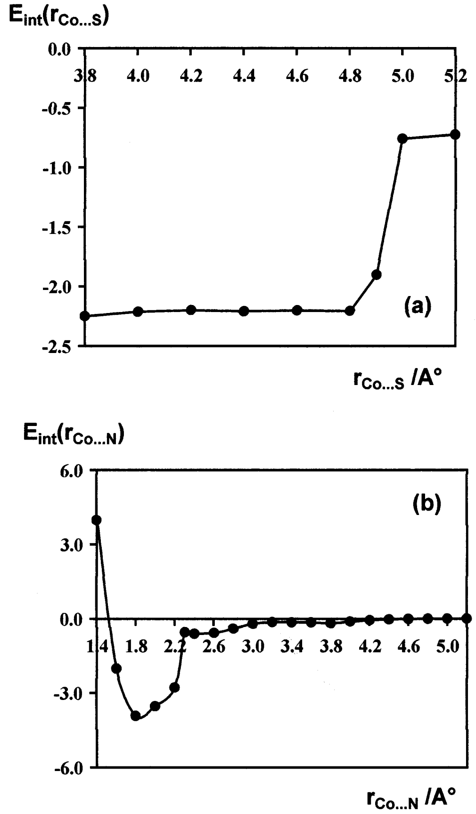

Figure 2. Interaction energy profile for the (a) CoPc···2ME and (b) CoPc···Py systems along the reaction coordinate.

If we adopt a molecular orbital viewpoint and use the "frozen core" assumption, where $d\rho = d\rho_{VALENCE}$, $f(\vec{r})$ can be identified with the electron density of the frontier molecular orbital involved.[25] Thus, as an approximation, the second right term appearing in eqs 4−6 is used for the Fukui function associated with the three different kinds of attacks as mentioned above. HOMO and LUMO are the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. These are just approximate rules for classical frontier orbital theory, as proposed by Fukui.[26−29] It is important to note that the Fukui function is a reactivity index based on the electronic density which has a physical meaning in contrast to the FMO (frontier molecular orbital) which does not. In the analysis of the Fukui function, we will use $f^-(\vec{r})$ which will be illustrated in terms of graphical maps.[30−32]

Results and Discussion

Global Properties. *Interaction Energy (IE).* The interaction energy profiles for the redox and formation reactions along the reaction coordinate were built up, and the results obtained are shown in Figure 2 parts a and b. Numerical values of IE for both systems are also included in Tables 1 and 2. For the redox reaction, we found that the IE profile is characterized by two regions, a minimum region in the range of $r_{Co\cdots S}$ = 3.8 Å → 4.8 Å and a no interaction region between $r_{Co\cdots S}$ = 5.0 Å → 5.2 Å. The values of the interaction energy between $r_{Co\cdots S}$ = 3.8 Å → 4.8 Å remain relatively constant about −2.2 eV. It can be seen that the stabilization energy from 5.0 Å to 4.8 Å is about −33 kcal/mol which is an indicative that a favorable interaction betwen CoPc and 2ME occurred. Note that the 4.9 Å value suggests that the interaction energy changes in a continuous way between the interaction region ($r_{Co\cdots S}$ = 3.8 Å → 4.8 Å) and the no interaction region ($r_{Co\cdots S}$ = 5.0 Å → 5.2 Å). In addition, the results obtained of the interaction energy for the CoPc···2ME system are not conclusive to differentiate between a net CT and a partial CT.

TABLE 1: Calculated Values for Interaction Energy (E_{int}, eV), Dipole Moment (μ, D), Atomic Net Charge (q, C), and Spin Density (ρ^s) for the CoPc···2ME System

$r_{Co\cdots S}$ (Å)	E_{int}	μ	q^{Co}	q^S	ρ^S (Co)	ρ^S (S)
3.8	−2.2491	1.0757	−0.4141	−0.0592	−0.00770	1.02448
4.0	−2.2123	1.6805	−0.4136	−0.0640	−0.00067	1.02536
4.2	−2.1984	1.7210	−0.4127	−0.0661	0.00049	1.02608
4.4	−2.2087	1.4989	−0.4108	−0.0691	0.00399	1.02482
4.6	−2.2005	1.9791	−0.4102	−0.0764	−0.00094	1.02477
4.8	−2.2051	2.0705	−0.4084	−0.0823	−0.00063	1.02671
4.9	−1.9011	1.8901	−0.3780	−0.0648	0.00761	1.02748
5.0	−0.7588	20.7588	−0.3330	−0.8666	−0.26442	−0.00186
5.2	−0.7239	22.1412	−0.3432	−0.8727	−0.25053	−0.00127

TABLE 2: Calculated Values for Interaction Energy (E_{int}, eV), Dipole Moment (μ, D), Atomic Net Charge (q, C), and Spin Density (ρ^s) for the CoPc···Py System

$r_{Co\cdots N}$ (Å)	E_{int}	μ	q^{Co}	q^N	ρ^S (Co)	ρ^S (N)
1.4	3.9788	3.8488	−0.4572	1.0589	−0.05571	−0.05389
1.6	−2.0131	6.1415	−0.3713	0.7265	−0.08304	−0.27097
1.8	−3.9197	7.7723	−0.3397	0.5284	−0.03519	−0.02901
2.0	−3.5305	7.7171	−0.3860	0.3764	−0.16027	0.01692
2.2	−2.7749	4.9663	−0.3357	0.1509	0.71750	0.07028
2.3	−0.5442	3.6060	−0.4136	0.1094	−0.29219	0.02780
2.4	−0.6028	3.5774	−0.3870	0.0839	−0.30154	0.01661
2.6	−0.5658	3.1731	−0.2859	0.0330	−0.45819	0.01582
2.8	−0.3939	2.9876	−0.2790	0.0023	−0.42040	0.00793
3.0	−0.2070	2.7011	−0.2791	−0.0229	−0.38344	0.00427
3.2	−0.1305	2.5002	−0.2777	−0.0413	−0.36329	0.00262
3.4	−0.1441	2.3434	−0.2786	−0.0530	−0.34653	0.00161
3.6	−0.1421	2.2315	−0.2793	−0.0602	−0.33587	0.00093
3.8	−0.1801	2.1713	−0.3152	−0.0642	−0.25924	0.00048
4.0	−0.1083	2.1221	−0.3106	−0.0677	−0.26747	0.00034
4.2	−0.0504	2.0797	−0.3116	−0.0699	−0.26511	0.00018
4.4	−0.0188	2.0471	−0.3125	−0.0713	−0.26354	0.00009
4.6	−0.0038	2.0243	−0.3134	−0.0723	−0.26224	0.00004
4.8	0.0034	2.0087	−0.3144	−0.0730	−0.26129	0.00002
5.0	0.0071	2.0069	−0.3154	−0.0735	−0.25993	0.00001
5.2	0.0090	1.9912	−0.3161	−0.0739	−0.25921	0.00000

In relation to the formation reaction for the interaction between CoPc and Py, Figure 2 shows that the profile has only one global minimum at $r_{Co\cdots N}$ = 1.8 Å with the presence of a covalent bond; therefore, the theoretical calculations predict that a partial CT is occurring in that point. The $r_{Co\cdots N}$ = 2.3 Å distance shows a small increment with respect to $r_{Co\cdots N}$ = 2.4 Å. The $r_{Co\cdots N}$ = 2.3 Å calculation shows one imaginary vibrational frequency (−97 cm^{-1}), which is indicative of a transition state geometry.

We conclude that the IE descriptor only gives the electronic structures that are thermodynamically favorable along a reaction coordinate, indicated by the presence of minimum points. In addition, the global IE descriptor does not provide enough information that allows us to distinguish between a partial and a net CT.

Dipole Moment. The calculated values of the dipole moment for both systems are also included in Tables 1 and 2. Figure 3, parts a and b, shows the dipole moment profile for both systems, CoPc···Py system and CoPc···2ME calculated for the reaction coordinates $r_{Co\cdots N}$ and $r_{Co\cdots S}$, respectively. For the CoPc···2ME system, we can see clearly two regions: one of them corresponds to the no interaction and the other associated to the minimum region for $r_{Co\cdots S}$ = 4.9 Å → 3.8 Å. The no interaction region between 5.2 and 5.0 Å can be understood as two charges being separated through space; that is, if the anion of 2ME has

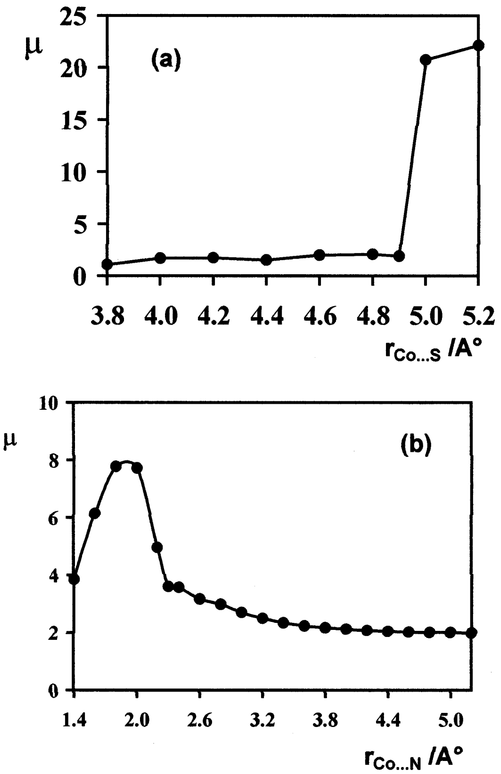

Figure 3. Dipole moment profile for the (a) CoPc···2ME and (b) CoPc···Py systems along the reaction coordinate.

only an electrostatic interaction with the CoPc residue, the dipole moment should be increased as both residues are separated from each other. The minimum region could be understood in terms of a new electronic distribution of the complete system, which may be due to electron transfer; that is, if the electron, initially in the 2ME anionic residue, is transferred to the CoPc residue, then 2ME changed from an anionic species to a radical uncharged species producing an important decrease in the value of the dipole moment.

For the CoPc···Py system, a linear trend with an increment of the dipole moment value as both residues approach each other can be observed for the 5.2 Å → 2.4 Å region. Because both pyridine and CoPc are uncharged species, if both systems are approaching each other they produce a polarization of each system that can be seen in a small increment of the dipole moment value; that is, for shorter distances, a greater polarization is observed. In the short distance region of 2.2 Å → 1.4 Å, a different behavior is observed because of the formation of the covalent bond.

Local Properties. *Spin Density* (ρ^s). Calculated values of the spin density for both systems are also included in Tables 1 and 2. Figure 4 shows the profiles obtained for the spin density calculated for the sulfur (S) and cobalt (Co) atoms of the redox reaction (CoPc···2ME) and for the nitrogen (N) and cobalt atoms of the formation reaction (CoPc···Py) along the reaction coordinate. As a graphical illustration, Figure 5 includes the surfaces of total spin density of the complete systems for some values of the reaction coordinate, where (a) is referred to the redox reaction and (b) indicates the formation reaction.

In the case of the redox reaction, Figure 4 shows that at long distances for the range between 5.2 Å → 5.0 Å the spin density for the sulfur atom is zero as expected for the closed shell thiolate anion. In contrast to this, the ρ^s value for the cobalt atom is different from zero, as expected for the paramagnetic cobalt(II) complex. Note that the positive value of ρ^s is obtained when the alpha spin predominates, and the negative value of ρ^s occurs if the beta spin predominates. Figure 5 indicates for this region that the spin density is localized in the CoPc residue. In the 4.9 Å → 3.8 Å region, an important change of the spin density value is observed for the sulfur and cobalt atoms. ρ^s is one for S and zero for Co. Because the total value of ρ^s for the complete CoPc···2ME system is one, it is possible to identify clearly through our results that a $RS^\bullet$ radical is being formed in that region of the reaction coordinate. Figure 5 illustrates for this region that the total spin density is completely localized on the sulfur atom of the 2-mercaptoethanol. These results suggest that a *net* CT occurred in the 4.9 Å → 3.8 Å region from the sulfur to the cobalt atom, i.e., the transfer of one electron.

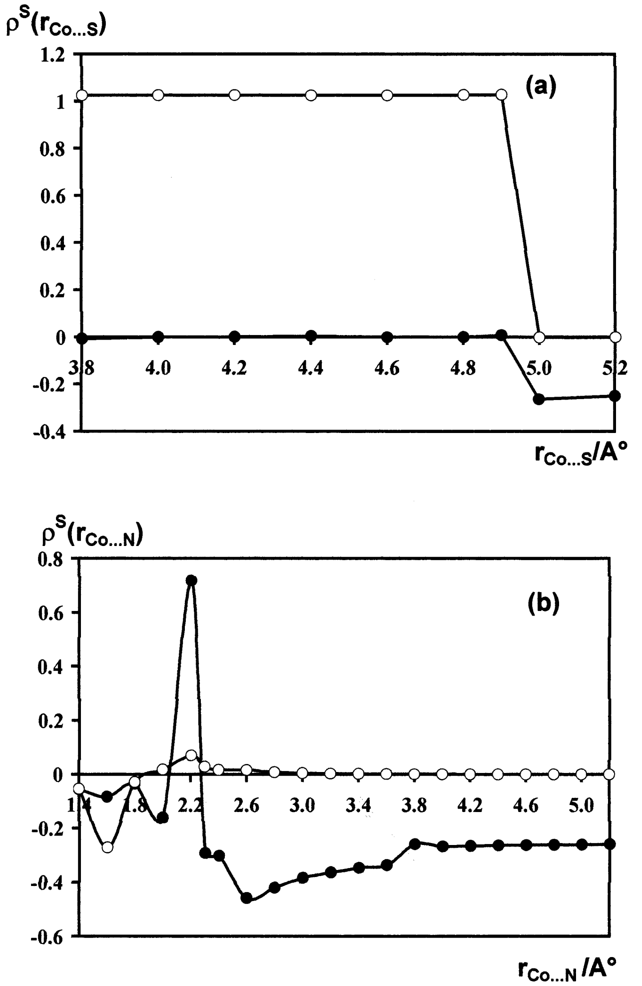

Figure 4. Spin density profile for (a) Co (●) and S (○) atoms for the CoPc···2ME system and (b) Co (●) and N (○) atoms for the CoPc···Py system, along the reaction coordinate.

In relation to the formation reaction, Figure 4 shows that the spin density presents a very constant behavior for the cobalt and the nitrogen atoms in the range 5.2 Å → 2.4 Å. It has a near zero value for N atom and differs from zero for the Co atom. Along this region, the total ρ^s is localized on the CoPc macrocycle as it is shown in Figure 5. In general, we observed that an increment in the ρ^s for the cobalt atom occurs when $r_{Co\cdots N}$ decreases, probably as a response to the interaction of both species, CoPc and Py, in the bond formation. One may conclude that the spin density is a good local descriptor of charge transfer because it allows us to identify clearly the position along a reaction coordinate where a *net* CT occurs, i.e., to differentiate between a net CT and a partial CT.

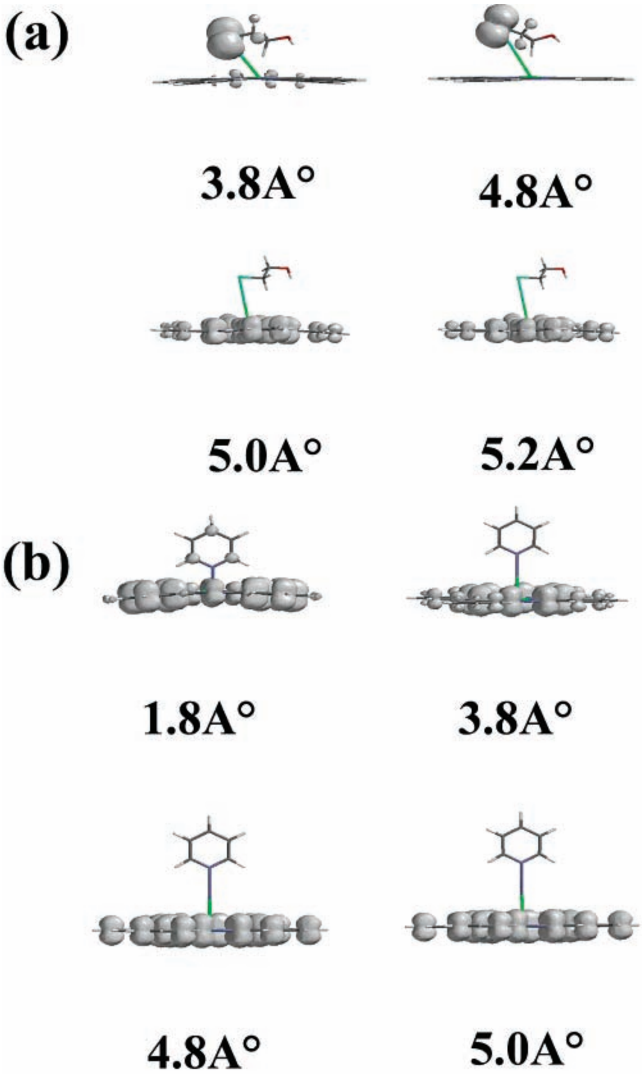

Figure 5. Spin density surfaces for (a) the CoPc···2ME system and (b) the CoPc···Py system, illustrated at selected distances.

Atomic Net Charge. Numerical values for both systems are also presented in Tables 1 and 2. The atomic net charges of the atoms involved directly in the charge-transfer process, sulfur (S), nitrogen (N), and cobalt (Co) atoms, were calculated. The profiles along the reaction coordinate for the atoms studied that belong to the CoPc···2ME system are shown in Figure 6a and the corresponding values for the CoPc···Py system are shown in Figure 6b. Note that the atomic charges derived from the NAO approximation were used.

For the CoPc···2ME system, in the no interaction region 5.2 Å → 5.0 Å, a negative value close to one is obtained for the sulfur atom as is expected for the thiolate anion. An important change in the value of the net charge on the sulfur atom is observed in the region 4.9 Å → 3.8 Å. A value near to zero is observed for this region as is expected for the thiolate radical. For the cobalt atom, an almost constant value is observed along the whole reaction coordinate. As expected for these systems where the transition metal is bonded to a very delocalized system, the net transfer of one electron (as seen by the analysis of spin density in the 4.9 Å → 3.8 Å region) is observed as an increment of the negative charge of the complete CoPc residue and not only for the cobalt atom.

For the CoPc···Py system, a different behavior is observed. The net charge for the nitrogen atom at 5.2 Å has a small negative value as expected for this atom in the pyridine ligand.

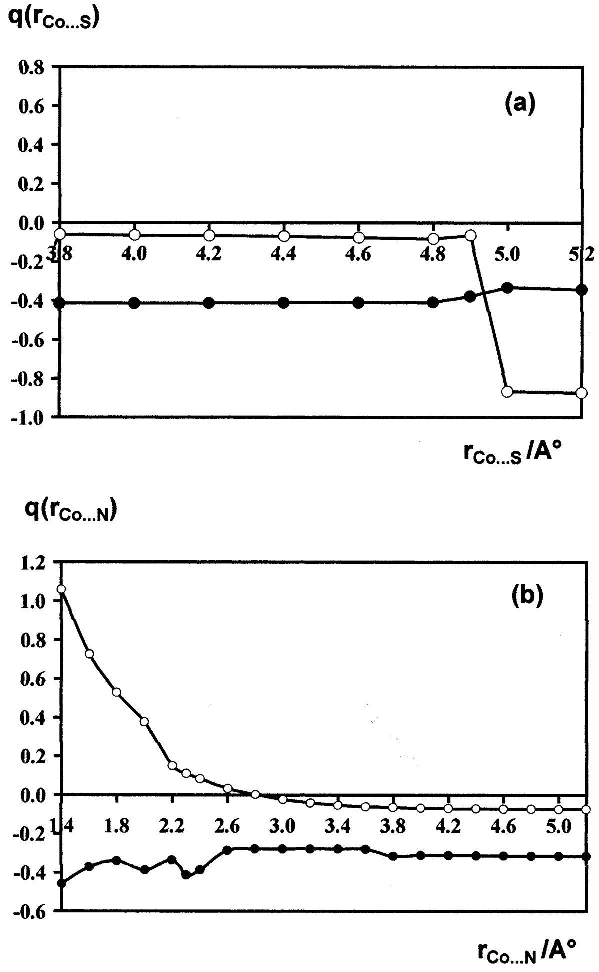

Figure 6. Atomic charge profile for (a) Co (●) and S (○) atoms for the CoPc···2ME system and (b) Co (●) and N (○) atoms for the CoPc···Py system, along the reaction coordinate.

As both residues (CoPc and Py) are getting closer from each other, the net charge of the nitrogen atom becomes more positive, as expected when a coordinate bond is formed. The net charge for the cobalt atom remains almost constant along the reaction coordinate, the same behavior as in the former system CoPc···2ME, as it was mentioned above. In addition, the net atomic charge profile for the CoPc···2ME system shows a dramatic change of this local property in the 4.8 Å → 3.8 Å range mainly for the sulfur atom. In contrast to this, the associated profile for the CoPc···Py system does not show any dramatic change along the reaction coordinate, as we could expect for a formation reaction.

Fukui Function. Figure 7 presents the results of the Fukui function $f^-(\vec{r})$ obtained from the theoretical calculations. Graphical maps of $f^-(\vec{r})$ are shown for some reaction coordinate values which correspond to the more representative points of the complete studied profile. Figure 7a illustrates the results obtained for the CoPc···2ME system and Figure 7b includes those corresponding to the CoPc···Py system. Note that the blue color in the surfaces indicates the largest value for $f^-(\vec{r})$, the yellow color represent an intermediate value, and the red color has a zero value. Because the $f^-(\vec{r})$ descriptor represents the most probable electrophilic region and therefore the most reactive site, we can analyze how that site varies along the reaction coordinate. In the former case, we observe (Figure 7a) that in the no interaction region, 5.2 Å → 5.0 Å, the preferred reaction site is localized on the sulfur atom. In fact, the sulfur atom is the most electron rich region of the 2-mercaptoethanol

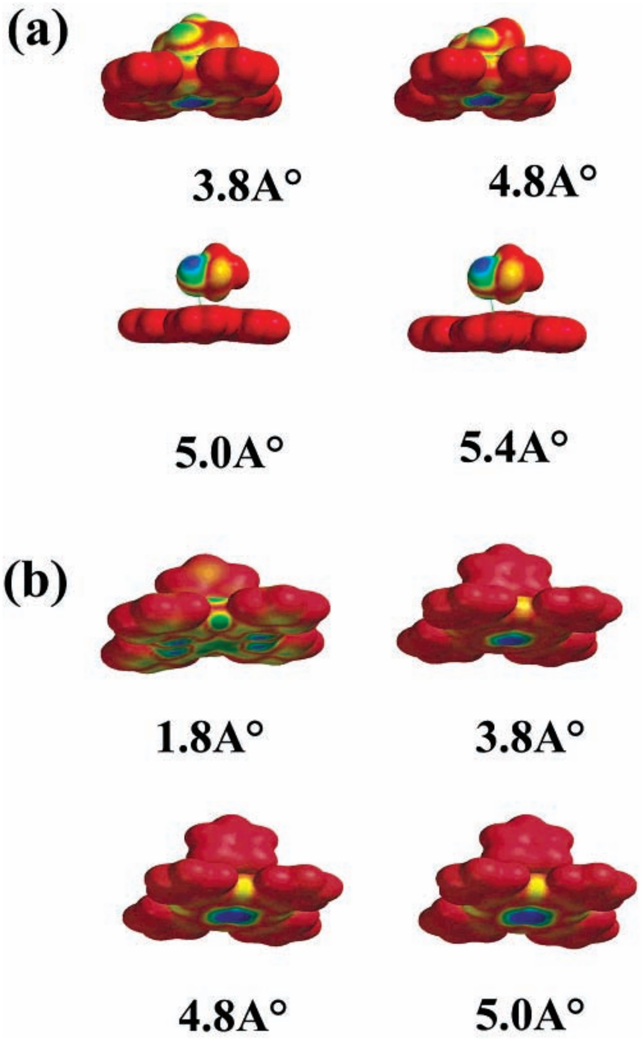

Figure 7. Fukui function $f^-(\vec{r})$ surfaces for (a) the CoPc···2ME system and (b) CoPc···Py system, illustrated at selected distances.

anion, and consequently, it is the electrophilic site of the system. However, when the reactants are approaching each other, that is, the 4.8 Å → 3.8 Å region, the Fukui function results show that the most reactive site is shifted to the position of the cobalt atom. The comparison between the $f^-(\vec{r})$ results for both regions, that is, 4.8 Å → 3.8 Å and 5.2 → 5.0 Å, indicates that a change in the electronic density distribution has occurred. The frontier electron is localized in the CoPc for the 4.8 Å → 3.8 Å region and in the sulfur atom for the 5.2 Å → 5.0 Å region. In particular, we found that the part of CoPc most electron rich is on the cobalt atom. The change produced between both regions is a response to the presence of an interaction between CoPc and 2-mercaptoethanol. These results allow us to state that a charge transfer has occurred, but we cannot discriminate between a partial CT or a net CT.

Figure 7b shows the results for selected points of the reaction coordinate for the CoPc···Py system. It can be seen that the most electron rich site is on the cobalt atom for all distances with the exception of the bond distance (1.8 Å). These results are in agreement with the interaction energy profile shown in Figure 2 for the CoPc···Py system in the sense that, if practically no interaction would exist between CoPc and pyridine, the frontier electron should be localized on a metallic atom, as we observed for the cobalt atom. Note that the Fukui function depicted in Figure 7b corresponds to the electronic density of the frontier molecular orbital SOMO, that is, $\rho_{SOMO}(\vec{r})$. When the interaction between CoPc and Py starts, it is expected that the SOMO should be a mixture between these molecules, and then $f^-(\vec{r})$ will tend to be more delocalized along the complete system than at a specific atom.

In addition, the Fukui function $f^-(\vec{r})$ results prove to be in agreement with the conclusion obtained from the spin density and atomic charges results in the sense that the 4.8 Å → 3.8 Å region is where a CT has occurred. However, although the Fukui function $f^-(\vec{r})$ is a charge-transfer descriptor it does not differentiate between a *partial* CT and a *net* CT.

Conclusions

We present theoretical results for the interaction of CoPc and two different substrates (2ME and Py) in the gas phase performed at a semiempirical calculation level parametrized for transition metals such as PM3(tm). Profiles of several global and local properties were calculated along the reaction coordinate through which the interaction occurs. We found that the global and local properties profiles are very different between CoPc···2ME (redox reaction) and CoPc···Py (formation reaction). In the case of the redox reaction, both global and local properties show the existence of two regions: the no interaction region localized for distances greater than 5.0 Å and the charge-transfer region localized for distances smaller than 4.8 Å. For the formation reaction, we found from the global and local properties that only one region is clearly defined, the bond formation region.

In particular, spin density and atomic net charge prove to be good descriptors for the *net* CT process (redox reaction) because they clearly indicate the frontier electron position along the system. The results of these properties show that a *net* CT occurs between 5.0 and 4.8 Å.

It is interesting to point out that the 4.9 Å distance was performed to investigate the abrupt changes region, i.e., how change the interaction energy and the others descriptors between 4.8 and 5.0 Å. The results in the interaction energy change suggests that we are facing a continuous interaction between CoPc and 2ME residue, however the dipole moment, spin density, and atomic net charge remain as an on−off property; that is, they show an abrupt change.

From the viewpoint of the calculation level, we conclude that PM3(tm) is a good method for the modeling of CT processes at a low computational cost.

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