The Oxidation of Thiols by Cobalt N_4−Complexes: a Correlation between Theory and Experiments

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Received: July 23, 2001; In Final Form: September 22, 2001

We present a theoretical study of the reactivity of some substituted porphyrins and phthalocyanines toward the electroxidation of 2-mercaptoethanol. The donor−acceptor intermolecular hardness and the electrophilicity index have been chosen indicators in order to discriminate the relative reactivity of the different species. All the calculations have been carried out using a recent hybrid Hartree−Fock/density functional approach (PBE0), and solvent effects have been introduced using a recent version of the polarizable continuum model (C-PCM). Our results show that azaporphyrin molecules are less reactive than the corresponding porphyrins in the gas phase. In contrast, solvation significantly affects the reactivity of the considered species, reversing the general trend. Our theoretical results are in agreement with the electrochemical experiments, carried out to further validate the computational predictions.

1. Introduction.

Metal complexes of N_4 ligands, such as porphyrins, are widely studied as biomimetic models for several biological redox processes, in particular for molecular oxygen transport and activation.[1] They are also well-known as efficient catalysts for oxidative degradation of various types of pollutants and residual wastes.[2] In the past decade, related complexes such as metallophthalocyanines were also reported to be efficient catalysts,[3] especially for the electrochemical oxidation of thiols.[4−6] Thus, modified electrodes coated by adsorbed or electropolymerized films made from these complexes have been extensively developed because they act as electrocatalysts by lowering particularly the overpotential of oxidation or reduction of the target molecules.[3−7] Reported studies related to the electrooxidation of thiols have shown that the catalytic activity of the adsorbed phthalocyanine-coated electrodes strongly depends on the nature of the central metal, with cobalt derivatives giving the best results.[4−6] But the mechanism of the electrocatalytic process is not well understood yet.

In a very recent study, we have extent the use of electropolymerized cobalt porphyrin film-coated electrode for the electrocatalysis of the oxidation of thiols.[8] We have shown, for the first time, that the cobalt porphyrin-modified electrode possesses a potential electrocatalytic activity for 2-mercaptoethanol electrooxidation. Its activity is significantly lower than that of the phthalocyanine-based one. Further extension of the use of various types of macrocyclic complexes, such as tetrabenzoporphyrin and porphyrazine, for the electrocatalytic activation of thiols may offer new alternatives in this field. A full theoretical understanding of the whole reaction mechanism is needed to fine-tune the experimental work.

In this context, the global descriptors of reactivity, as electronic chemical potential (μ) and chemical hardness (η),[9−11] represent a simple way to rationalize the different chemical behavior of similar species. In particular, μ characterizes the escaping tendency of electrons from the equilibrium system, while η can be seen as a resistance to charge transfer. These two entities are global properties of the investigated systems, and the characterization of their profiles along a reaction coordinate has been shown to be useful to study their chemical reactivity.[12−17] More recently, Parr and co-workers[18] have introduced another index, electrophilicity (ω), as a convenient parameter for assessing the electrophilicity power of an atom or molecule. This electrophilicity index can be defined in term of hardness and chemical potential.[18] Although the environment (i.e., solvent) plays an important role in most of the reactions, very few studies have been done for understanding its effects on the reactivity descriptors.[16,17,19]

From a more theoretical point of view, the hardness and softness concepts receive a rigorous definition in the framework of density functional theory (DFT), allowing their nonempirical evaluation and accurate calculation (see, for instance, refs 12 and 13). The accurate calculation of the hardness and chemical potential requires an accurate evaluation of the system's ionization energy and electron affinity. As for other molecular properties, DFT is an invaluable tool, if an adequate exchange-correlation functional is used. A number of functionals based on the generalized gradient approximation (GGA) have been developed in the past few years.[20,21] For example, fitting parameters to some set of experimental data and fulfilment of physical constraints are common approaches for developing new functionals.[21] In this contest, the Perdew−Burke−Erzerhof (PBE) exchange-correlation functional[22] is a particular approach since it contains no parameters fitted to experimental data. The PBE generally provides results which are at least comparable to those obtained with more empirical functionals.[23,24] Casting PBE in a particular hybrid model, where a predefined amount of Hartree−Fock (HF) exchange is added self-consistently to the DFT contribution,[25−27] leads to an even more accurate functional.[25,27,28] A number of tests have shown that by using this hybrid model (hereafter referred to as PBE0), the calculated ionization potentials, electronic affinities, and a number of other

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10.1021/jp012801+ CCC: $20.00 © 2001 American Chemical Society
Published on Web 11/22/2001

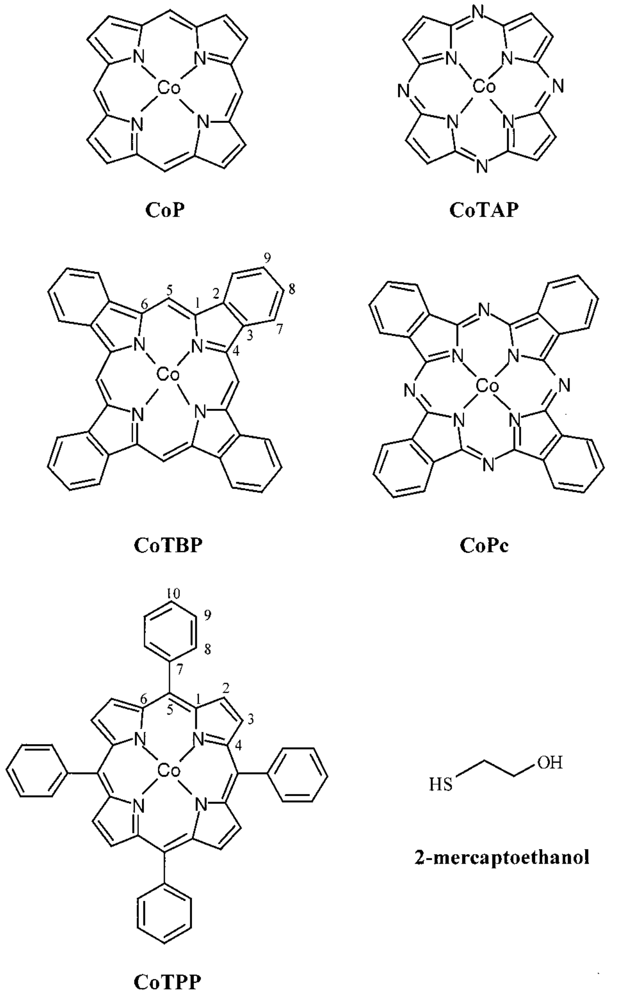

Figure 1. Sketches and atom labeling of the molecular systems considered in the present paper: Co(II) porphyrin (CoP), Co(II) tetraphenylporphyrin (CoTPP), Co(II) tetrabenzoporphyrin (CoTBP), Co(II) tetraazaporphyrin (CoTAP), Co(II) phthalocyanine (CoPc), and 2-mercaptoethanol.

electronic properties are remarkably close to experimental values.[27,29,30]

In this work, we apply the PBE0 approach to correlate the reactivity of a series of cobalt(II) N_4−ligands (see Figure 1), namely, Co(II) porphyrin (CoP), Co(II) phthalocyanine (CoPc), Co(II) tetraphenylporphyrin (CoTPP), Co(II) tetrabenzoporphyrin (CoTBP), and Co(II) tetraazaporphyrin (CoTAP), toward the electrocatalytic oxidation of 2-mercaptoethanol. This study is aimed at understanding the differences in activity experimentally observed for such compound.[4−6,8] To this end, the chosen set of molecules, characterized by a similar backbone, should give detailed information about the effects of substituents and different chemical environments on the reactivity and electron transfer properties. We have applied the notions of hardness, chemical potential, intramolecular hardness, and electrophilicity to better quantify these effects and discriminate between the examined molecular complexes. Furthermore, since solvent could strongly modified the electronic properties of such molecules, we have also considered solute−solvent interactions through the introduction in our Hamiltonian of a continuum solvation model.[31] Finally, theoretical results have been partially confirmed by an experimental kinetic investigation of the electrocatalytic oxidation of 2-mercaptoethanol (2-ME) with adsorbed CoTPP and CoPc on vitreous carbon electrode in 0.5M NaOH aqueous solution.

2. Computational Details

All DFT calculations were carried out with our modified version of the Gaussian 98 code,[32] using a recent hybrid Kohn−Sham/Hartree−Fock (KS/HF) model referred to as PBE0.[28] This approach is obtained casting the PBE exchange and correlation functional[22] in an hybrid scheme HF/DFT, where the HF exchange ratio (1/4) is fixed a priori.[33]

Two different basis sets have been used. The small set is composed of the CEP-121 pseudopotentials and basis (contraction [8s8p6d/4s4p3d]) for the Co atom and of the 6-31G(d) basis for C, N, O, S, and H.[34] It has been showed that such a basis set provides accurate geometrical parameters for metal−porphyrins.[35] A larger basis set has been also used, taking the 6-311G(d,p) basis sets for the lighter atoms and adding one p polarization function (exp = 0.08) to the CEP-121 basis for the metal atom.[36]

Each stationary point found was characterized as minimum or first-order saddle point by computing the harmonic vibrational frequencies.

Solvent effects were evaluated using the polarizable continuum model (PCM).[31] In particular, optimized structures and solvation energies have been computed by a cavity model, namely, the united atoms topological model (UATM),[37] coupled to the conductor-like polarizable continuum model (CPCM).[38] This approach provides results very close to those obtained by the original dielectric model for high dielectric constant solvents, but it is significantly more effective in geometry optimizations and less prone to numerical errors arising from the small part of the solute electron cloud lying outside the cavity (escaped charge effects).[38]

The definition of the hardness (η) was given by Parr and Pearson,[9,10] and a three-point finite difference approximation leads to the following working definition:

$$\eta = (I - A) \tag{1}$$

where I and A are the first vertical ionization potential and electron affinity of the neutral molecule, respectively. Analogously, the electronic chemical potential (μ) can be defined as:

$$\mu = -\frac{1}{2}(I + A) \tag{2}$$

Starting from these two quantities, the electrophilicity index (ω) was defined by Parr and co-workers[18] as:

$$\omega = \frac{\mu^2}{2\eta} \tag{3}$$

This expression may be regarded as a quantitative formulation of the model of Maynard et al., which introduced the concept of “electrophilicity power” of a ligand as a measure of its electron saturation.[39]

In a next step, the donor−acceptor intermolecular hardness (η_{DA}) can be defined as:

$$\eta_{DA} = (I_D - A_A) \tag{4}$$

where A_A is the electron affinity of the acceptor A (A is here the macrocyclic complex) and I_D the vertical ionization energy of the donor molecule D (D is here the thiol, namely, 2-mercaptoethanol).[40,41] This concept compactly states the classical principle of electron-transfer reaction: “transfer of electrons from D to A is faster the closer in energy the highest occupied molecular orbital (HOMO) of D is to the lowest unoccupied molecular orbital (LUMO) of A”.[42] It is important to mention that η_{DA} represents the hardness of the initial system (A + D) by considering the isolated acceptor and the donor species, where the charge transfer has still not occurred and therefore gives a general idea on their reactivity. Nevertheless, the intramolecular hardness as reactivity index has been successfully used for the study of intermolecular charge-transfer reactions of electrochemical interest (see, for instance, ref 43).

The extension of these indexes (ω, χ, η) to the study of reactions involving open-shell systems (like those considered here) is straightforward (see, for instance, refs 10b, 12, and 13). Only, Koopmans' theorem cannot be used unambiguously to determine η and ω in term of the energies of the HOMO and LUMO for unrestricted wave functions. So we have calculated the ionization potentials and the electron affinities as the differences between the energies of the reference molecule (N electron system) and the corresponding $N + 1$ or $N - 1$ electron systems at the geometry of the reference species. All these latter calculations, i.e., the evaluations of the energies of the N, $N + 1$, and $N - 1$ electron systems, have been carried out with the 6-311+G(d,p) basis set for light atoms and the polarized CEP-121G basis for Co.

Finally, the electronic structure of these molecules have been investigated using the natural bond orbital (NBO) approach and the related natural population analysis (NPA).[44] The NPA approach is particularly effective also for inorganic complexes, since it gives a description of the electronic distribution which is less sensitive to the computational parameters (e.g., basis set).[44] These computations have required the writing of a proper interface between the Gaussian 98 package and the last public release of the NBO program.[45]

3. Experimental Section

The working electrode was a vitreous carbon disk electrode from Radiometer-Tacussel (France) exposing a geometrical area of 0.071 cm^2 and mounted in Teflon. It was polished before each experiment with 3 and 0.3 μm alumina pastes, followed by extensive rinsing with ultrapure Milli-Q water. The electrochemical experiments were carried out with a conventional three-electrode cell and a PAR-263A potentiostat/galvanostat (U.S.A.). Platinum wire was used as counter electrode and a calomel saturated electrode, sce, as the reference electrode. Electrolytic solutions were routinely deoxygenated with argon.

CoPc and CoTPP were adsorbed on the vitreous carbon electrode by placing on its surface a drop of a 1 mmol/L solution of the complex in dimethylformamide or acetonitrile, respectively, for 60 s. After this, the electrode was rinsed with ethanol.

CoPc and CoTPP were obtained from Aldrich (U.S.A.) and used as provided. All other products were reagent grade and used as received.

4. Results and Discussion

As mentioned in the Introduction, we have considered a series of Co(II)$-$N$_4$ macrocycles, acting as electron acceptors and characterized by different substitution on position 5 (methyne, nitrogen, or phenyl), and one donor molecule, namely, 2-mercaptoethanol. The optimized geometrical parameters of the acceptor molecules (see Figure 1) are reported in Tables 1 and 2. All the geometries have been computed using an unrestricted KS approach and by considering the spin state $S = {}^1/_2$. Before discussing in details these results, some remarks on the spin-contamination problems should be recalled. Indeed, it is well-known that he interpretation of the expectation value for S^2, $\langle S^2\rangle$, is not straightforward in the framework of DF methods (see for instance ref 46). Nevertheless, its value still indicates, at least roughly, the extent of contamination by higher spin states. In our case, the computed PBE0 values are always $\langle S^2\rangle < 0.77$, thus suggesting that we are dealing with essentially pure doublet states.

TABLE 1: Main Geometrical Parameters (Å and Deg) of Co(II) Porphyrin (CoP) and Co(II) Tetraazaporphyrin (CoTAP)[a]

	CoP			CoTAP	
	small basis	large basis	exp[b]	small basis	large basis
CoN	1.979	1.978	1.967(3)	1.901	1.902
NC1	1.371	1.369	1.371(3)	1.368	1.366
C1C2	1.436	1.435	1.435(4)	1.449	1.447
C2C3	1.356	1.354	1.357(4)	1.353	1.350
C1X5	1.381	1.379	1.383(3)	1.321	1.319
CoNC1	127.5	127.5	127.47(17)	126.9	126.8
NC1X5	125.3	125.4	125.18(20)	127.5	127.5
NC1C2	111.0	110.9	110.64(22)	110.1	110.0
C1C2C3	106.5	106.6	106.75(25)	106.8	106.8
C1X5C6	124.3	124.3	124.73(22)	121.3	121.3

[a] All values have been computed at the PBE0 level using two different basis sets: (a) CEP-121G on Co and 6-31G(d) on C,N and H (small basis), (b) CEP-121Gp on Co and 6-311G(d,p) on C,N and H (large basis). [b] Ref 48.

All the molecules have a planar rearrangement for the porphyrin ring (D_{4h} symmetry), in agreement with experimental data.[47-49] The only exception is represented by TPP: in this case, the cycle is significantly distorted from planarity, with the typical ruffling of the skeleton ring[50] (see Figure 2), due to the strong steric interactions of the phenyl rings.[51] The calculated gas-phase structures are in excellent agreement with the experimental data (see Tables 1 and 2), all the bond lengths, and valence angles, being determined within the expected error for the chosen method (error on bonds $\leq$ 0.01 Å, error on valence angle $\leq$ 0.9°). Greater discrepancies are found for the CoN distances, which are systematically overestimated at the PBE0 level, the error ranging between +0.004 (CoPc) and +0.020 Å (CoTBP). Our calculations reproduce well the experimental trends on the geometries observed along the series. Among others, we notice that the cobalt$-$pyrrole distance increases by replacing the nitrogen atoms bridged to pyrrole by a methine group. This distance is 1.901 Å in CoTAP and 1.979 Å in CoP (+0.08 Å), and the same increase can be found in going from CoPc to CoTBP (1.923 and 2.004 Å, respectively). This latter value well compare with the experimental deviation (+0.07 Å). This enlargement of the central hole upon substitution is, of course, directly related to the greater steric effect of the lone-pair electrons of the nitrogen atom with respect to that of the methane hydrogen atom.[49,52] The CoTPP complex shows a different behavior, due its twisted structure.

The extension of the basis set has essentially no effect on the geometries of all the considered complexes, the maximum variation being $-$0.004 Å on bond lengths and +0.4° on valence angles. This suggests that the small basis set already provides geometrical parameters at convergence.

The electronic structure of Co(II) N$_4$ complexes have been described in details in a number of papers:[52-55] for all the macrocycles, the ground electronic state is a doublet, corresponding to the $^2A_{1g}$ state in D_{4h} symmetry, with the unpaired electron lying in the d_{z^2} atomic orbital of Co. In Table 3 are collected the natural population analysis (NPA) charges for the whole series. Although the metal atom has a formal charge of +2 in the neutral N$_4$ complex forms, all the NPA atomic charges are around 1.0 $|e^-|$, thus pointing out the covalent character of the metal$-$ligand bonding. There is a striking difference between the macrocycles which have a porphyrin-like ring (CoP, CoTBP,

TABLE 2: Main Geometrical Parameters (Å and Deg) of Co(II) Tetraphenylporphyrin (CoTPP), Co(II) Tetrabenzoporphyrin (CoTBP), and Co(II) Phtalocyanin (CoPc)[a]

	CoTPP			CoTBP			CoPc		
	small basis	large basis	exp[b]	small basis	large basis	exp[c]	small basis	large basis	exp.[d]
CoN	1.965	1.964	1.949(1)	2.004	2.003	1.984(5)	1.923	1.923	1.919(1)
NC1	1.374	1.372	1.380(2)	1.370	1.370	1.376(7)	1.371	1.369	1.380(3)
C1C2	1.442	1.440	1.433(2)	1.448	1.445	1.447(8)	1.450	1.449	1.457(7)
C2C3	1.352	1.350	1.354(2)	1.401	1.398	1.401(8)	1.398	1.396	1.398(1)
C1X5	1.391	1.388	1.386(2)	1.373	1.375	1.383(8)	1.317	1.314	1.325(1)
C3C7	–	–	–	1.399	1.396	1.393(8)	1.392	1.390	1.397(1)
C5C7	1.490	1.490	1.488(2)	–	–	–	–	–	–
C7C8	1.400	1.396	1.395(2)	1.390	1.384	1.372(9)	1.390	1.387	1.396(1)
C8C9	1.392	1.390	1.387(2)	1.401	1.404	1.389(9)	1.406	1.403	1.410(1)
C9C10	1.395	1.392	1.388(2)	–	–	–	–	–	–
CoNC1	127.4	127.3	127.7(1)	126.6	126.8	127.5(4)	126.3	126.2	126.50(78)
NC1X5	126.2	126.2	126.5(1)	126.0	125.8	124.7(6)	127.8	127.7	127.93(24)
NC1C2	110.6	110.6	110.4(1)	110.5	110.7	111.7(5)	110.0	109.9	110.14(21)
C1C2C3	106.8	106.8	107.0(1)	106.0	106.0	105.8(5)	106.3	106.3	106.38(8)
C1X5C6	122.8	123.0	123.4(1)	124.8	125.0	125.6(6)	122.1	122.1	107.00(9)
C4C3C7	–	–	–	132.8	133.1	133.9(6)	132.3	132.3	132.06(57)
C3C7C8	–	–	–	117.7	118.1	118.1(6)	117.4	117.4	117.06(17)
C7C8C9	120.6	120.5	120.6(1)	121.4	121.1	121.7(6)	121.3	121.3	121.36(27)
C8C9C10	120.1	120.1	120.0(1)	–	–	–	–	–	–
C9C10C9	119.8	119.8	119.9(1)	–	–	–	–	–	–

[a] All values have been computed at the PBE0 level using two different basis sets: (a) CEP-121G on Co and 6-31G(d) on C,N and H (small basis), (b) CEP-121Gp on Co and 6-311G(d,p) on C,N and H (large basis). [b] Ref 50; [c] Ref 49; [d] Ref 46.

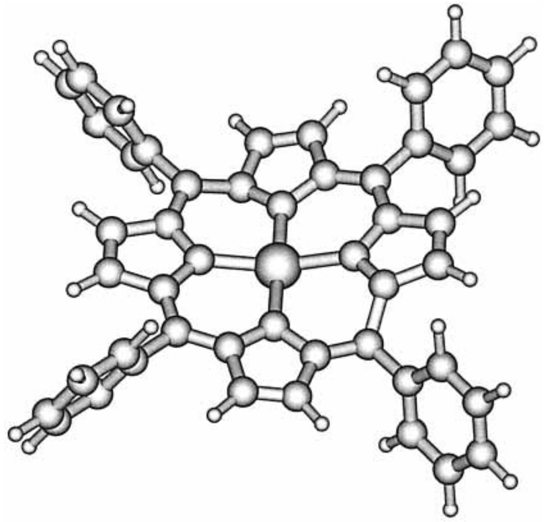

Figure 2. Structure of the Co(II) tetraphenylporphyrin (CoTPP).

and CoTPP) and the "tetra-azo porphyrins" (CoTAP and CoPc). In fact, the substitution of the less electronegative methylene carbon atoms in the pyrrole-bridging position with the more electronegative nitrogen significantly alters the electronic structure. Of course the greatest effects are for the atoms in position 5 (N5 or C5), which have a charge of about −0.25 in the first case and −0.46 C in the second. Also, the C1 atoms are significantly affected (+0.40 vs +0.16/0.19 $|e^-|$). Small variations are found on the N atoms bonded to the metal or on the same Co atoms (about +1.20 $|e^-|$ in CoP and +1.08 $|e^-|$ in CoTAP). Here the small differences found within the series regard the occupation of the d orbitals. In particular, the d_{z^2} has a small excess of electron density ($d_{z^2}^{1.02}$) in all the complexes, while difference are found for the in-plane $d_{x^2-y^2}$ orbital. This latter has a smaller occupation in the methyne-substituted molecule (CoP, CoTBP) than in the nitrogen complexes (CoTAP, CoPc). Interestingly, CoTPP is closer to nitrogen, the configuration being $d_{z^2}^{1.03}d_{x^2-y^2}^{0.74}$.

Neutron diffraction studies allow for an estimation of the charge density on the central Co and, in particular, of the d orbital electron population.[47,50,56] A quantitative comparison between our NBO analysis and the experimental results (obtained through a least-squares fitting of the density) cannot be rigorous, since the procedure for the division of the total electron density is different.[47] Nevertheless, the agreement of the PBE0 calculations with the experiments is qualitatively satisfactory. For instance, the X-ray analysis of the CoTPP gives a density corresponding to $d_{z^2}^{0.92}d_{x^2-y^2}^{0.83}$, close to our values.[51] Slightly different values are found from neutron experiments, $d_{z^2}^{1.21}d_{x^2-y^2}^{0.21}$. The apparent discrepancy observed for the $d_{x^2-y^2}$ orbital comes from the fact that neutron experiments are not sensitive to the population of this metal−ligand bonding orbital in which electron spins are mostly paired.[52]

As mentioned above, we have considered the effect of bulk solvent (here water) on the electronic properties of Co(II) complex by the CPCM model.[31] While this approach reproduces the nonspecific solute−solvent interactions well, specific (e.g. H-bond) effects are only partially mimicked.[57,58] In our case, solvent (water) molecules strongly coordinated to the cobalt atom might significantly affect the electronic properties of the solute. Nevertheless, we thought that no significant changes in the general trends can be expected from these interactions, due to structural similarities along the molecular series. Furthermore, it should be noticed that even if the electrophile/nucleophile interactions, like that reported in the present paper, might be assumed to be preceded by a desolvation step, it is expected that this desolvation process may not be complete and that partial solvation may affect these interactions to some extent.[59] In short, the PCM model should give an idea about the effects of bulk solvent on the electronic properties of such macrocycles. A similar solvent model has been applied by Truhlar and co-workers in a recent theoretical work on oxidation potential of substituted anilines.[60]

In Table 4 are reported the PBE0 geometries in aqueous solution, obtained using the small basis set. These geometries have been obtained with the small basis set. As it can be seen from these data, the solvent has a marginal effect on the geometries, the largest differences with the gas-phase parameters being ±0.05 Å. A slightly significant effect can be expected on the electronic distributions. In particular, there is an increase

TABLE 3: Natural Population Analysis for All the Considered N_4 Macrocycles[a]

	gas-phase					solution				
	CoP	CoTAP	CoTBP	CoPc	CoTPP	CoP	CoTAP	CoTBP	CoPc	CoTPP
Co	1.116	1.076	1.119	1.097	1.093	1.112	1.096	1.132	1.114	1.109
N	−0.596	−0.641	−0.576	−0.629	−0.603	−0.609	−0.634	−0.582	−0.634	−0.613
C1	0.160	0.402	0.189	0.441	0.185	0.149	0.400	0.181	0.438	0.182
C2	−0.264	−0.252	−0.068	−0.089	−0.253	−0.260	−0.260	−0.077	−0.096	−0.259
X5	−0.254	−0.458	−0.264	−0.487	−0.059	−0.250	−0.481	−0.270	−0.507	−0.063
C7	–	–	−0.215	−0.164	−0.061	–	–	−0.226	−0.171	−0.062
C8	–	–	−0.242	−0.197	−0.229	–	–	−0.249	−0.202	−0.233
C9	–	–	−0.242	−0.197	−0.241	–	–	−0.249	−0.202	−0.244
C10	–	–	–	–	−0.244	–	–	–	–	−0.244

[a] All the values have been computed in gas-phase and in aqueous solution at the PBE0 level, using the CEP-121/6-31G(d) basis set and the corresponding optimized geometries.

TABLE 4: Main Geometrical Parameters (Å and Deg) for All the Considered N_4 Macrocycles in Aqueous Solution Using the CEP-121G/6-31G(d) Basis Set

	CoP	CoTAP	CoTBP	CoPc	CoTPP
CoN	1.983	1.899	2.005	1.921	1.977
NC1	1.370	1.362	1.368	1.365	1.373
C1C2	1.438	1.454	1.446	1.453	1.440
C2C3	1.361	1.355	1.400	1.402	1.352
C1X5	1.382	1.316	1.378	1.311	1.389
C3C7	–	–	1.399	1.391	–
X5C7	–	–	–	–	1.492
C7C8	–	–	1.389	1.387	1.401
C8C9	–	–	1.407	1.402	1.392
C9C10	–	–	–	–	1.395
CoNC1	127.3	127.1	126.4	126.7	127.5
NC1X5	126.0	126.4	125.9	126.6	126.2
NC1C2	110.7	110.8	110.3	109.6	110.8
C1C2C3	106.6	106.3	106.1	105.9	106.7
C1X5C6	123.5	123.0	125.3	123.0	122.6
C4C3C7	–	–	132.9	132.0	–
C3C7C8	–	–	117.9	117.5	–
C7C8C9	–	–	121.1	121.0	120.6
C8C9C10	–	–	–	–	120.1
C9C10C9	–	–	–	–	119.8

TABLE 5: Main Geometrical Parameters (Å and Deg) for the Anion of the 2-Mercaptoethanol, Computed Either in the Gas Phase or in Aqueous Solution[a]

	gas-phase		solution	
	small basis set	large basis set	small basis set	large basis set
SC	1.821	1.823	1.836	1.834
CC	1.519	1.515	1.517	1.514
CO	1.439	1.438	1.421	1.422
OH	0.967	0.959	0.977	0.970
SCC	112.6	113.0	112.4	112.5
CCO	113.6	113.2	108.5	108.3

[a] All values have been computed using two different basis sets: 6-31G(d) (small basis) or 6-311G(d,p) (large basis).

of the charge separation within the molecule, with an increase of the positive charge brough by the metal atom and of the negative charge over the ring. This effect, which corresponds to a stabilization of the LUMO, is larger in the more polarizable tetra-azo complexes than in the methyne series.

As concerning the donor molecule, we have considered in this study the anionic form of 2-mercaptoethanol, namely, $[HOCH_2CH_2S]^-$, to simulate experimental conditions (basic medium). The optimized geometries, obtained in the gas-phase and in aqueous solution, are reported in Table 5. As for the macrocycles, the geometry is practically unaffected by the basis extension. In contrast, nonspecific solvent interactions, due to the strong effect on the charged species, induce some variations on geometry. In particular, the largest variations are on the polar CO and CS bonds, which are elongated of 0.02 Å in going from the gas phase to the aqueous solution. All the other bonds do not experience the effect of the solvent. The modification induced by the solvent on the electronic structure of the anion are well evidenced by the NPA charges. For instance, the O charge increases from −0.78 to −0.80 $|e^-|$ in going from gas phase to aqueous solution, while even the greatest effect affects the sulfur atom: from −0.73 to −0.84 $|e^-|$. This corresponds to a strong stabilization of the HOMO (a p orbital on S) upon solvent interaction.

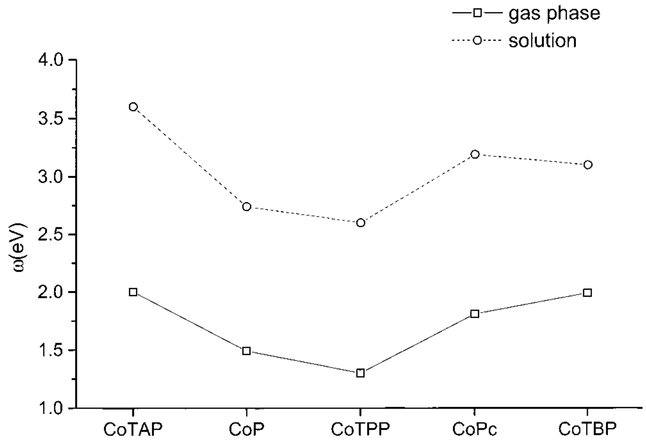

Figure 3. Plots of the electrophilicity power (ω, eV) in the gas phase and in aqueous solutionfor the five systems under investigation.

In summary, our calculations show that the PBE0 model describe well the molecular and electronic structure of such a class of complexes, and it makes us confident about its interpretative/predictive strength.

As mentioned above, reactivity index provide an quantitative measure of some intuitive chemical concepts, as electron/charge transfer or electrophilicity. In particular, we have chosen two reactivity indexes, ω and η_{DA}: the first one is an "intramolecular" parameter, depending only on the electronic characteristic of the acceptor species, while the second one, being defined on the acceptor and donor properties, is an "intermolecular" parameter. So, these two indexes should give a complete picture of the oxidation process. The obtained values for the electrophilicity index are reported in Figure 3. Since this index quantifies the tendency of a molecule to "soak up" electrons, the higher the electrophilicity index is, the greater the propensity of the complex will be to attract electron from a generic donor molecule. All the considered macrocycles show comparable ω values, ranging from 2.0 (CoTAP) to 1.3 eV (CoTPP). In particular, CoTAP has a ω value significantly higher than that of the corresponding porphyrins (CoP and CoTPP), due to the electron-withdrawing effect of the nitrogen atoms in position 5. In contrast, CoPc and CoTBP have close ω values, thus

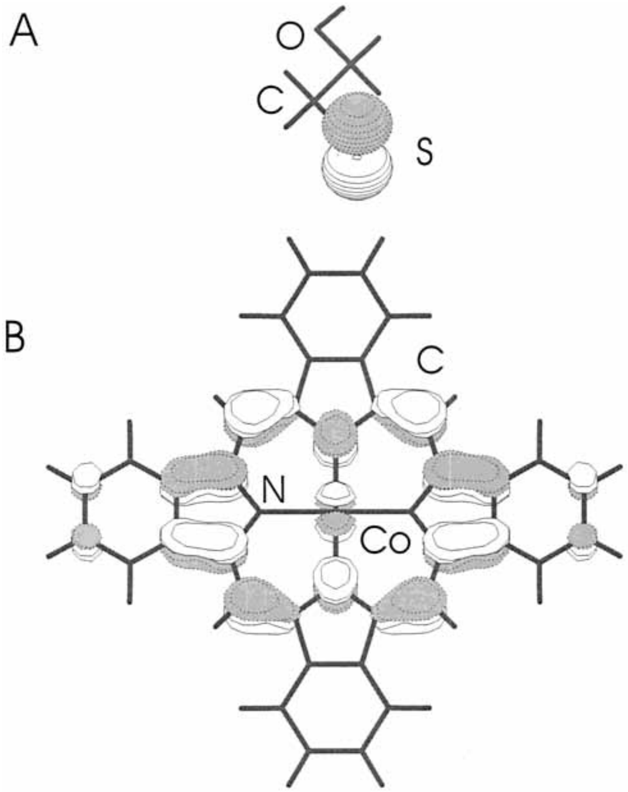

Figure 4. Shape of the frontier molecular orbitals involved in the oxidation: (a) HOMO of the mercaptoethanol anion; (b) LUMO of the Co(II) phthalocyanine.

TABLE 6: Donor−Acceptor Intramolecular Hardness (η_{DA}, eV) of the Considered N_4 Systems[a]

molecule	gas phase	solution[b]	solution
CoTAP	3.26	2.36	2.34
CoP	2.36	3.20	3.18
CoTPP	2.34	3.22	3.28
CoPc	2.98	2.52	2.50
CoTBP	2.34	3.22	3.26

[a] The values have been calculated either in the gas phase or in aqueous solution. [b] Computed using gas-phase geometries.

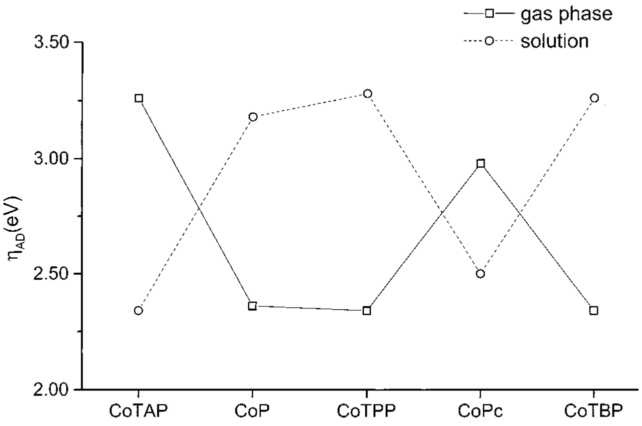

Figure 5. Plots of the intramolecular donor−acceptor hardness (η_{ad}, eV) in the gas phase and in aqueous solution for the five systems under investigation.

underling the major role played by the benzene rings in storing electrons. The solvent strongly rules the magnitude of the calculated electrophilicities but does not significantly alter the overall trend. In fact, in going from the gas phase to aqueous solution, CoTAP still has the highest ω value (3.6 eV) and CoTPP the lowest one (2.6 eV). Only the CoPc is slightly more electrophilic than CoTBP in aqueous solution, in contrast with the vacuum findings. These significant variations, observed in condensed phase, are related to a strong change of the chemical hardness which significantly decreases from gas phase to solution, while the chemical potential is much less affected.[19]

The calculated electrophilicity indexes suggest that azaporphyrins have a greater capacity to accept electrons from a generic electron donor and, consequently, they would be more active in the oxidation reaction of 2-mercaptoethanol. This trend is significantly enhanced, but not changed, by the interactions with a polar solvent.

Transfer of electrons from a donor D to an acceptor A is facilitated when the HOMO of D is close in energy to the LUMO of A. In our case, D is the anion of the 2-mercaptoethanol, and the acceptors are the complexes of Co(II). The orbitals involved in this interaction are a p orbital localized on sulfur atom for D and a π* for all the macrocycles (see Figure 4). This latter has a significant contribution from the d_π orbital of the Co and possess the appropriate symmetry to interact with the HOMO of the donor.

The intramolecular donor−acceptor hardness (η_{DA}), as defined by eq 3, provides a more rigorous description of this nucleophile/electrophile interactions. The η_{DA} values for the whole series of N_4 macrocycles are collected in Table 6 and plotted in Figure 5. We recall that a low value for the hardness suggests to a greater interactions between donor and acceptor species, corresponding to a small energy gap between the donor HOMO orbital and the LUMO of acceptor. Some trends appears from the analysis of our gas-phase values (first column of Table 6). In particular, we can observe that the porphyrin-like macrocycles (CoP, CoTBP, and CoTPP) are predicted as the most reactive species, all showing similar η_{DA} (about 2.4 eV). Higher hardness' are instead found for the aza compounds, CoPc and CoTAP (3.0 and 3.2 eV, respectively). This result can be rationalized in terms of the relative energies of the donor and acceptor orbitals. In fact, the electron-withdrawing substituent (nitrogen atom in azaporphyrins) in position 5 of the macrocycles significantly stabilizes the SOMO, whereas the contrary is true for electron-donating substituent (methylene group). Since the HOMO of the thiol is quite high in energy, CoTAP and CoPc show higher hardness. It is also interesting to note that the main contributions to the LUMO come from the atoms belonging to the inner porphyrin ring so that substituents on pyrrole has no significant effects. For instance, CoP and COTBP have similar hardness. The same holds for CoTPP, since there is no contribution from the orbitals of the phenyl groups, almost orthogonal to the N_4 plane.

The solvent has a drastic effect on the hardness, as can be seen from the values reported in the last columns of Table 6. In particular, the η_{DA} for CoP and CoTBP change from 2.4 to 3.2 eV, in going from gas phase to aqueous solution. Similar variations, but in the opposite directions, are also found for the aza compounds. It is also noteworthy that CoTAP is predicted to be slightly more reactive than CoPc (2.4 vs 2.6 eV).

Two main effects are responsible for these results. First of all, the anion of 2-mercaptiol, being a charged species, is strongly stabilized by the electrostatic interactions with the solvent, and the energy of its HOMO significantly drops down. At the same time, azaporphyrins are more polarizable than porphyrins (having higher dipole moments) so that they strongly experience the reaction field generated by the continuum. The net effect is a complete inversion of the prediction in going from the gas phase to the aqueous solution. It is interesting to note that electron withdrawing groups, even though they

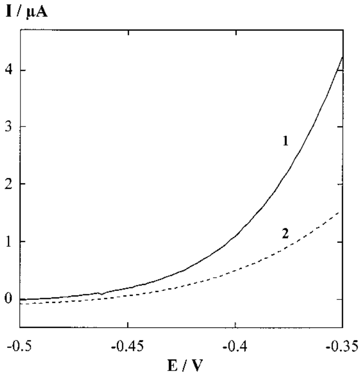

Figure 6. Rotating disk voltammetry for the electrooxidation of 1 mmol L^{-1} of 2-mercaptoethanol on adsorbed CoPc (curve 1) and adsorbed CoTPP (curve 2) on vitreous carbon electrode (area of 0.071 cm^2) in 0.5 mol L^{-1} NaOH aqueous solution. (Potential scan rate, 10 mV/s; electrode rotation speed, 1600 rpm.)

decrease the electron density on the cobalt center (see Table 3), also contribute to reduce the gap between the energy of the SOMO of the macrocycle and the HOMO of the thiol, thus decreasing the reactivity index. Finally, similar results are obtained using gas phase or solution geometries, since these latter are not significantly altered by solvent (see Table 6, last column).

In summary, the two reactivity indexes provide coherent and complementary information about the reactivity of the different species. In fact, both indexes point out that azaporphyrins are more reactive than the corresponding porphyrins, due to the presence of the electronegative (and more polarizable) nitrogen atoms in the inner ring. Nevertheless, the electrophilicity index alone does not allow to unambiguously distinguish between the different species. Moreover, bulk solvent effects control to some extent the reactivity of such species, even in the absence of any specific solute−solvent interactions. Work is in progress to investigate in more details the role of the first solvation shell in the electro-oxidation reactions.[61]

Preliminary experiments have been carried out in order to evaluate the theoretical prediction of the reactivity of some of the examined complexes and to verify the drastic change found in going from gas phase to solution phase. In particular, experimental kinetic investigations of the electrocatalytic oxidation of 2-mercaptoethanol (2-ME) at adsorbed CoTPP and CoPc on vitreous carbon electrode, in 0.5 M NaOH aqueous solution has been performed. It has been recently shown that the intramolecular hardness provides reliable predictive analysis for similar inner-sphere electrochemical reaction kinetics involving substituted metallophthalocyanines adsorbed on electrode surfaces.[62] Figure 6 shows the obtained rotating disk electrode voltammograms showing the apparition of a large anodic current as soon as -0.45 V/sce, which is related to the electrocatalytic oxidation of 2-ME at the adsorbed CoTPP and CoPc modified electrodes.[4,6,8] By assuming that the oxidation reaction is pseudo-first-order in 2-ME, the apparent rate constant can be calculated as $k = j/nF$[2-ME] where j is the kinetically controlled current density measured at a given potential located at the lowest polarization range (to avoid mass transport correction), $n = 1$, and [2-ME] $= 1$ mmol L^{-1}. The calculations, at -0.4 V/sce give log k (cm s^{-1}) $= -3.48$ and -4.15 for CoPc and CoTPP, respectively. These results show that log$k$ increases as the chemical hardness η_{DA} of the acceptor−donor system decreases, as predicted by the theoretical calculation when bulk solvent effects are taken into account.

4. Conclusion

In this paper, we have applied a recent DFT method to analyze the differences in reactivity observed for a family of N_4 macrocycle toward 2-mercaptoethanol. Both intramolecular hardness and electrophilicity have been used as reactivity indexes to discriminate between the different species, and calculations have been carried out either in the gas phase and in aqueous solution. Our results show that the values of the electrophilicity index suggest that azaporphyrins could have a greater capacity to accept electrons from a donor and, consequently, to be more active in the oxidation reaction of 2-mercaptoethanol. This trend is enhanced by the interactions with a polar solvent. The intramolecular hardness index shows that azaporphyrins molecules are less reactive than the corresponding porphyrins in the gas-phase, while the reverse is true in aqueous solution. These calculations predict a reactivity trend in agreement with experimental data, obtained from electrochemical measurements in aqueous solution. The remarkable result that should be emphasized from this study is that the reactivity indexes can be considered a reliable tools in the prediction of the reactivity trends, especially when coupled to a realistic electronic simulation, including environmental (e.g., solvent) interactions.

Acknowledgment. The authors are grateful to Professor J. H. Zagal (Universidad de Santiago de Chile) and Dr. I. Ciofini (University of Fribourg) for helpful discussions and for proving a pre-print of reference 62.

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