



A theoretical approach to a chemical system convertible into a storage cell: carbon–carbon bonds functioning as electron donor and electron acceptor units

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Density functional calculations have been performed on nickel Schiff base complexes and nickel porphyrinogen complexes in order to understand the behaviour of these systems in redox processes. In nickel Schiff base complexes C–C σ bonds are formed upon reduction, while in nickel porphyrinogen complexes C–C σ bonds are formed upon oxidation. In both systems the formation or the cleavage of C–C bonds avoids a variation in the oxidation state of the metal. The lack of variation in the oxidation state of the metal is the first step towards the reversibility of the redox process. The complementary behaviour in redox processes of nickel Schiff base complexes and nickel porphyrinogen complexes can be considered in a reversible electrochemical cell with the discharge process based on C–C bonds breaking and the recharge based on C–C bonds formation. © 2003 Elsevier Science B.V. All rights reserved.

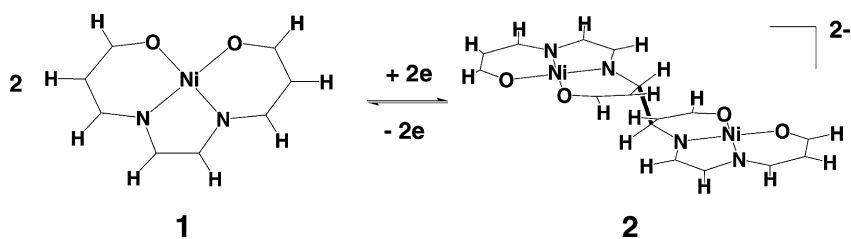
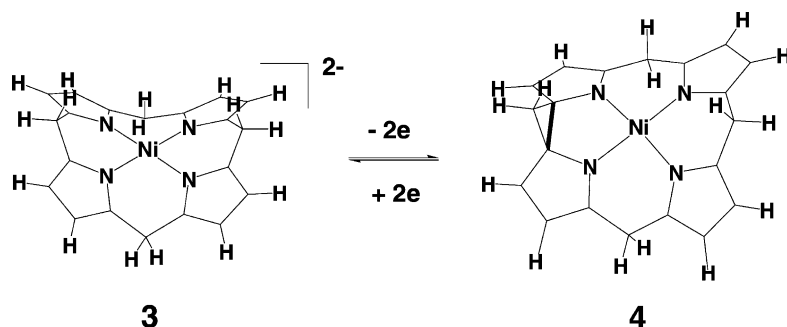
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1. Introduction

We have recently investigated [1–3] the mechanisms by which we can store and release electrons through the formation or the breaking of C–C σ bonds. We can consider two main classes of compounds: (i) transition metal Schiff base complexes where the C–C σ bond formation is the result of a reductive process, as shown in [Scheme 1](#); and (ii) porphyrinogen complexes where the C–C σ bond formation is the result of an oxidative process, as depicted in [Scheme 2](#).

Recently, Floriani and co-workers investigated [4] the possibility of coupling these two classes of complexes, considering nickel as transition metal, in order to have the constituents of a storage cell. The present paper is focused on density functional calculations on model systems of the above mentioned classes of compounds. [Ni(salophen)] (salophen = *N,N'*-phenylenebis(salicylideneaminato)dianion) was considered as a model for the oxidized form of a transition metal Schiff base complex, while [Ni(porphyrinogen)]²⁻ was considered as a model for the reduced form of a porphyrinogen complex. In order to make the calculations feasible, some simplifications have been made in the investigated systems. In particular, in the salophen the aromatic rings were substituted by C=C double bonds, while in the

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Scheme 1. C–C σ bond formation upon a reductive process.Scheme 2. C–C σ bond formation upon an oxidative process.

porphyrinogen the ethyl *meso* groups were replaced by hydrogen atoms. Previous studies [2–3] suggest that these simplifications should not affect significantly the electronic distribution around the transition metal and the C–C σ bond formation and breaking mechanisms.

The main goal of our work is the evaluation of the overall redox reaction energy in order to give an estimate of the electrochemical potential of the storage cell.

2. Computational details

Density functional theory (DFT), which has been found to be a very cost effective method to study transition metal systems [5], has been used for the determination of equilibrium geometries and the evaluation of the energetics of all the investigated systems and processes. All calculations were carried out using the Amsterdam density functional (ADF) program package [6–10]. The program is characterized by the use of a density fitting procedure to obtain accurate Coulomb and exchange potentials in each SCF cycle, by accurate and efficient numerical integration of the

effective one-electron Hamiltonian matrix elements [11,12] and by the possibility to freeze core orbitals. The molecular orbitals were expanded in an uncontracted double- ζ STO basis set for all atoms with the exception of 3d and 4s Ni orbitals for which we used a triple- ζ STO basis set. This basis set was augmented by one 4p function for Ni, one 2p polarization function for hydrogen and one 3d polarization function for the other elements. The cores (Ni: 1s–2p; C, N, O: 1s) have been kept frozen. The BP86 exchange–correlation functional was used for all the calculations. This functional is based on Becke’s functional [13] and includes Slater exchange along with corrections that involve the gradient of the density for the exchange potential together with the local gradient-corrected correlation functional proposed by Perdew [14].

3. Model systems and geometry optimization

Molecular structures were optimized at the BP86 level of theory [13,14]. We investigated the model systems shown in Schemes 1 and 2. As already mentioned, in order to make the calculation feasible, the

salophen ligand in the nickel Schiff base complexes was simplified replacing the aromatic rings with C=C double bonds. In the porphyrinogen complexes, the *meso* groups are ethyl groups and they must be different than hydrogen in order to avoid the conversion of the porphyrinogen into a porphyrin; however, from an electronic point of view, we do not expect to find a very different situation when the *meso* groups are ethyls or hydrogens. For this reason we considered hydrogens instead of ethyls. The geometry of the model systems considered was fully optimized starting from parameters deduced from the available experimental X-ray structures [4]. The counterions were not considered explicitly in the model systems. We considered C_{2v} symmetry for **1**, C_i for **2**, C_2 for **3** and C_s for **4**. **1** and **4** are neutral species, while **2** and **3** are dianionic species, since we did not include the alkali metal counterions in the calculation. The optimised geometries of all the investigated systems are available from the authors on request.

4. Results and discussion

The optimized structure of the oxidized form of the nickel Schiff base model system investigated, **1**, is shown in Fig. 1.

We will denote this species $[\text{Ni}(\text{salophen}')]$, in which salophen' indicates the simplified form of salophen we have considered in our model systems. The coordination around the transition metal is planar, as

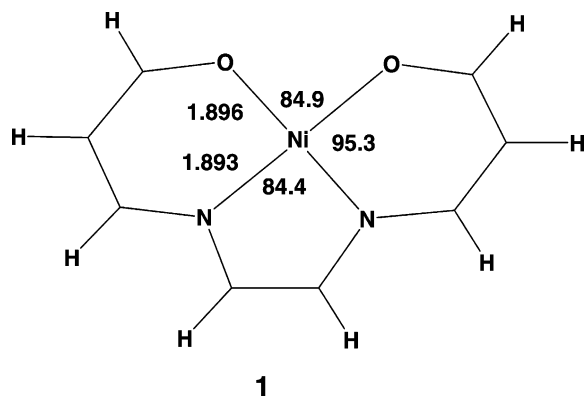


Fig. 1. Optimised structure of $[\text{Ni}(\text{salophen}')]$ (**1**). Only the main geometrical parameters are shown. Bond lengths in angstroms, angles in degrees.

Table 1

Total energies (eV) relative to atoms of the investigated systems.

Species	Symmetry	Energy
$[\text{Ni}(\text{salophen}')]$ (1)	C_{2v}	-132.25
$[\text{Ni}(\text{salophen}')_2]^{2-}$ (2)	C_i	-264.95
$[\text{Ni}(\text{porphyrinogen}')_2]^{2-}$ (3)	C_2	-270.23
$[\text{Ni}(\text{porphyrinogen}')]$ (4)	C_s	-266.92

expected. The total energy, computed with respect to the atoms, of **1** is reported in Table 1. The reduction by two electrons of the monomeric species **1** gives rise, through the reductive coupling of the imino groups, to the dimeric species **2**, $[\text{Ni}(\text{salophen}')_2]^{2-}$, whose optimised structure is reported in Fig. 2 and total energy in Table 1.

We can notice that the reduction does not affect significantly the coordination around the transition metal: the Ni–O bond lengths indeed become slightly longer passing from 1.896 to 1.900 and 1.921 Å, while the Ni–N bond lengths change from 1.893 to 1.894 and 1.928 Å. The bond angles around the nickel do not change appreciably. This is in agreement with the fact that the metal does not change its oxidation state, as it is suggested by the Mulliken population analysis. The main variation upon reduction is the formation of a C–C σ bond of 1.617 Å between carbon atoms of imino groups of the two original salophen' ligand. This bond distance is comparable with that computed previously for similar complexes of titanium [2], niobium [3] and molybdenum [3] and is slightly longer than the X-ray value observed for $[\text{M}_2(\text{salophen}_2)(\text{Na})_2(\text{thf})_6]$ [1] with $\text{M} = \text{Ti}$ (1.605 Å) and V (1.585 Å).

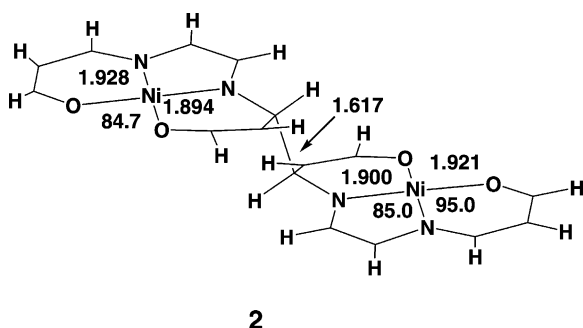


Fig. 2. Optimised structure of $[\text{Ni}(\text{salophen}')_2]^{2-}$ (**2**). Only the main geometrical parameters are shown. Bond lengths in angstroms, angles in degrees.

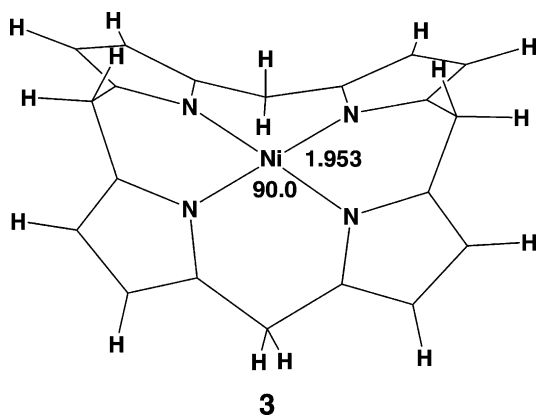


Fig. 3. Optimised structure of $[\text{Ni}(\text{porphyrinogen}')^{2-}]$ (**3**). Only the main geometrical parameters are shown. Bond lengths in angstroms, angles in degrees.

The optimised structure of $[\text{Ni}(\text{porphyrinogen}')^{2-}]$ species **3** is shown in Fig. 3, while its total energy is reported in Table 1.

Porphyrinogen' denotes the simplified form of porphyrinogen we have considered in our model systems. From Fig. 3 we see that the presence of the metal in the middle of the N_4 core of the porphyrinogen gives rise to an almost planar structure, because of the presence of the four Ni–N bonds. The oxidation by two electrons of species **3** gives rise to $[\text{Ni}(\text{porphyrinogen}')]$, **4**, whose optimised structure is shown in Fig. 4 and its total energy is reported in Table 1.

Also in this case, we do not observe significant variations in the coordination of the nickel, while we observe a strong rearrangement in the ligand, the oxidation leading to the formation of a cyclopropane ring in it. In this system the ligand shows a strong geometry rearrangement due to the formation of the cyclopropane ring. The strain in the structure is very high as it is suggested by the energies reported in Table 1. The instability of porphyrinogen complexes with cyclopropane rings have been previously observed [2,15]. Moreover, the calculations do not take into account the important energy contribution coming from the solvation of the counter cations by the solvent and the porphyrinogen itself. In many such derivatives the counter cation is η^3 , η^5 strongly bound to the pyrrolyl anions. This energy contribution of course should be responsible for an even larger endothermicity of the reaction shown in Scheme 2. The Mulliken population analysis

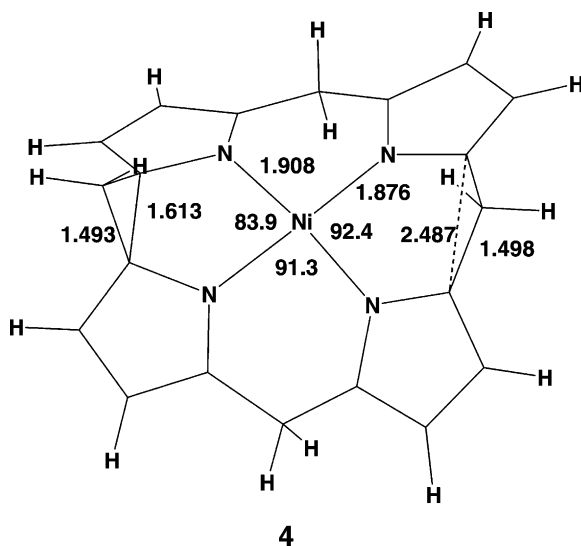
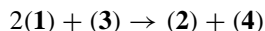


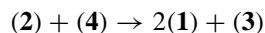
Fig. 4. Optimised structure of $[\text{Ni}(\text{porphyrinogen}')]$ (**4**). Only the main geometrical parameters are shown. Bond lengths in angstroms, angles in degrees.

suggests also in this case that we do not have a variation in the oxidation state of the metal, the oxidation being localized on the ligand through the formation of a C–C σ bond of 1.613 Å. This value is comparable with the value of 1.609 Å, previously computed [2] for the similar system $[\text{Ti}(\text{porphyrinogen}')^{4+}]$.

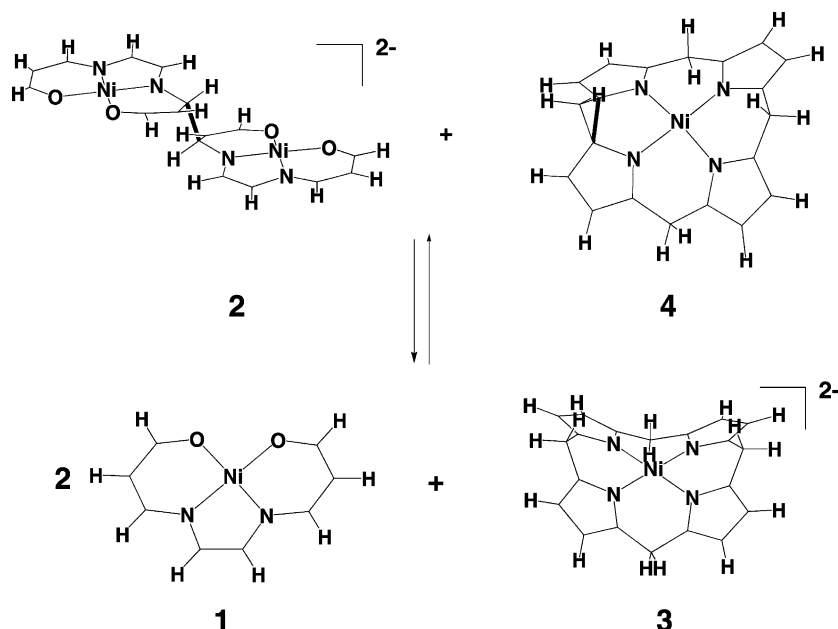
$[\text{Ni}(\text{salophen}')]$ and $[\text{Ni}(\text{porphyrinogen}')]$ show therefore a complementary behaviour upon redox processes: the first system indeed gives rise to the formation of C–C σ bonds upon reduction, while the second one shows a similar behaviour upon oxidation. Moreover **1** and **3** can be seen as the partners of a redox reaction, whose products are **2** and **4**:



Let us consider the reverse of this reaction, as it is reported in Scheme 3:



From the energies listed in Table 1 this reaction is computed to be exothermic and its ΔE is equal to $-275.9 \text{ kJ mol}^{-1}$. A rough estimate of the standard voltage of this redox reaction, assuming $\Delta G^\circ \approx \Delta E$, is $\Delta V \approx 1.4 \text{ V}$. The above reaction can be considered in an electrochemical cell, whose functioning is based on C–C bond breaking. Half-reaction $(\mathbf{4}) \rightarrow (\mathbf{3})$ is the



Scheme 3. An electrochemical cell based on C–C bonds breaking.

cathode of the cell, while half-reaction $(2) \rightarrow 2(1)$ is the anode of the cell. While the discharge of the cell implies C–C bonds cleavage, its recharge gives rise to formation of C–C bonds. It is worth noting that the important energy contributions coming from the solvation of the counter cations by the solvent and the porphyrinogen or the Schiff base, which should render the reaction reported in Scheme 1 more exothermic and the reaction shown in Scheme 2 more endothermic, in the overall reaction should cancel each other almost completely.

5. Conclusion

The present study at density functional level has shown that nickel Schiff base complexes and nickel porphyrinogen complexes show similar, although complementary, behaviour in redox processes. In nickel Schiff base complexes C–C σ bonds are formed upon reduction, while in nickel porphyrinogen complexes C–C σ bonds are formed upon oxidation. In both systems, however, the formation or the cleavage of the C–C bonds avoids a variation in the oxidation state of the metal. The lack of variation in the oxi-

dation state of the metal is the first step towards the reversibility of the redox process. The complementary behaviour in redox processes of nickel Schiff base complexes and nickel porphyrinogen complexes can be considered in a reversible electrochemical cell with the discharge process based on C–C bonds breaking and the recharge based on C–C bonds formation. The evaluation of the total energies of the systems investigated suggests that such an electrochemical cell presents an electrochemical potential suitable for practical applications.

Acknowledgements

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References

- [1] F. Franceschi, E. Solari, C. Floriani, M. Rosi, A. Chiesi-Villa, C. Rizzoli, *Chem. Eur. J.* 5 (1999) 708.
- [2] M. Rosi, A. Sgamellotti, F. Franceschi, C. Floriani, *Chem. Eur. J.* 5 (1999) 2914.

- [3] C. Floriani, E. Solari, F. Franceschi, R. Scopelliti, P. Belanzoni, M. Rosi, *Chem. Eur. J.* 7 (2001) 3052.
- [4] F. Franceschi, E. Solari, R. Scopelliti, C. Floriani, *Angew. Chem. Int. Ed.* 39 (2000) 1685.
- [5] A. Ricca, C.W. Bauschlicher, *J. Phys. Chem.* 98 (1994) 12899.
- [6] ADF Program System Release 2.3.0, <http://www.scm.com>.
- [7] E.J. Baerends, D.E. Ellis, P. Ros, *Chem. Phys.* 2 (1973) 42.
- [8] E.J. Baerends, P. Ros, *Chem. Phys.* 2 (1973) 51.
- [9] E.J. Baerends, P. Ros, *Chem. Phys.* 8 (1975) 41.
- [10] E.J. Baerends, P. Ros, *Int. J. Quantum Chem.* S12 (1978) 169.
- [11] P.M. Boerrigter, G. te Velde, E.J. Baerends, *Int. J. Quantum Chem.* 33 (1988) 87.
- [12] G. te Velde, E.J. Baerends, *J. Comput. Phys.* 99 (1992) 84.
- [13] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [14] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822;
J.P. Perdew, *Phys. Rev.* 34 (1986) 7046.
- [15] P. Belanzoni, M. Rosi, A. Sgamellotti, L. Bonomo, C. Floriani, *J. Chem. Soc., Dalton Trans.* (2001) 1492.