"Ab Initio" Calculations on a Novel Mode for Storing and Releasing Electrons via C–C Bond Formation and Cleavage

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Ab initio Hartree–Fock and second-order Möller–Plesset calculations have been performed on systems which can be viewed as models for [Ni(salophen)] and its reductive product. The results indicate that the metal does not change its oxidation state in the reductive process because no orbitals, localized on nickel and at low energy, are available to accept electrons, except the in-plane d orbital, whose occupation would imply a large increase in the repulsion. The "added" electrons prefer to form a C–C bond, which can be cleaved restoring the original product. Ni^{2+} is electrostatically bonded to the ligand and acts as a shield among the negative charges of the ligand itself. Correlation effects influence the energetic balance of the reductive process but not as heavily as expected for transition metal systems because the electronic distribution at the transition metal ion does not change in the reaction.

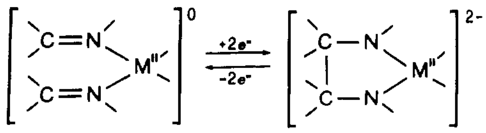
Introduction

There are a number of molecules which can function as electron storage and release systems. Coordination compounds on the "inorganic site" and the polyaromatic hydrocarbons on the "organic site" can be an exemplification. The variation of the electronic configuration for a transition metal and the use of π^* antibonding orbitals are the two mechanisms operating. The two classes of compounds mentioned above have significant limitation on the number of electrons which can be stored and in the fact that a significant difference in energy exists among the electrons possibly transferred. A number of problems have to be solved in this context in order to design molecules functioning as batteries.[1]

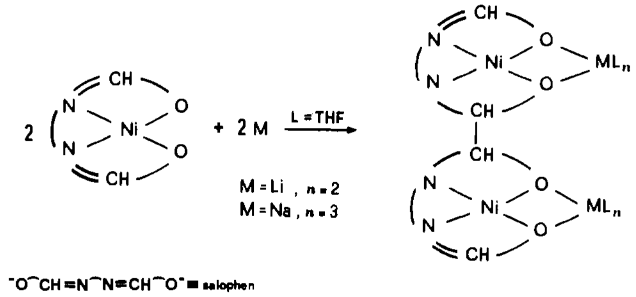
We should find a different mechanism for storing electrons in pairs. This should avoid the inconvenience mentioned above and make available a significant number of electrons. Some major classes can be envisaged at present, i.e., polyoxo derivatives having electrons in excess of those necessary for the existence of the skeleton.[2]

The present paper is focused on theoretical calculations on a novel class of compounds in which the storage and release of pairs of electrons is made possible by the formation and cleavage of carbon–carbon single bonds (Scheme I). Such a chemically very old reaction (pinacolinic-type reduction) can be made reversible and so functioning as an electron storage and release unit, which may be incorporated in rather complex structures. This is exemplified by the reduction chemistry of [Ni(salophen)],[3] [V(salophen)],[4] and [Zr(salophen)][5] [salophen ≡ *N,N'-o*-phenylenebis(salicylideneaminato) dianion] leading to the formation and cleavage of C–C σ bonds across two units (Schemes II and III). This leads either to the formation of dimers[3–5] or polymers,[3,5] allowing the storage of one pair or several pairs of electrons, respectively. The C–C bonds form by the chemical or electrochemical addition of two electrons, and when formed, they are able to reduce substrates by transferring the two electrons very far from the storage center.

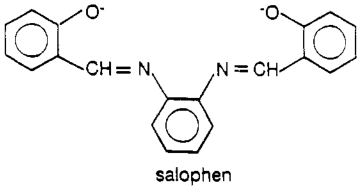
Scheme I



Scheme II



Scheme III



In order to carry out a theoretical ab initio investigation on molecules behaving as molecular batteries, some simplifications of the real systems have been considered: (i) the intramolecular reductive coupling of two imino groups of a tetradentate ligand leading to a C–C π bond (Scheme IVA); (ii) the intramolecular reductive coupling of two imino groups belonging to two different bidentate ligands binding the same nickel ion forming a C–C σ bond (Scheme IVB); (iii) the intermolecular reductive coupling of two imino groups belonging to two different tetradentate ligands

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(1) Floriani, C. *Centenary Lecture*: Royal Society of Chemistry: London, 1989.

(2) Carofiglio, T.; Floriani, C.; Sgamellotti, A.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.*, in press.

(3) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 756. Gambarotta, S.; Urso, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 3966.

(4) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1984**, 116.

(5) Solari, E.; De Angelis, S.; Floriani, C. Manuscript in preparation.

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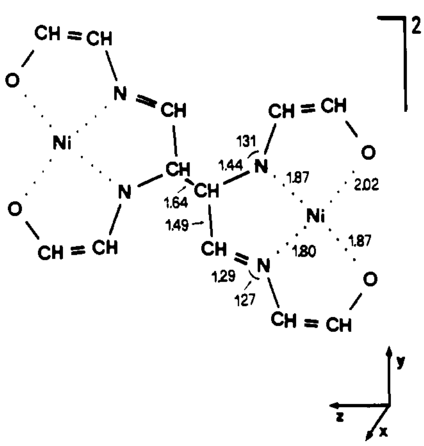
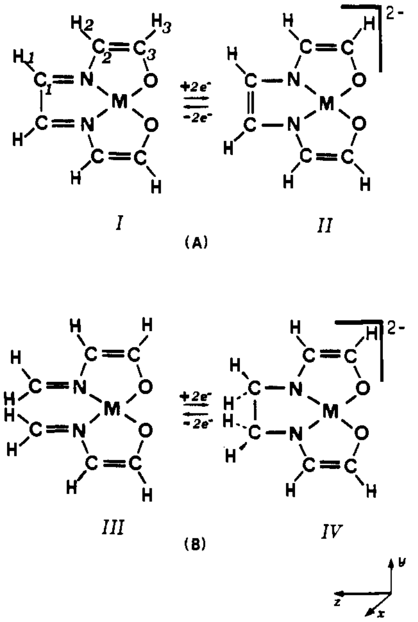


Figure 1. Geometry (in Å and deg) adopted for the dimer species.

Scheme IV



leading to a C–C σ bond (Figure 1). The last one is the closest model to the [Ni(salophen)] complex. Ab initio self-consistent-field (SCF) and second-order Möller- Plesset (MP2) calculations have been performed on these simplified systems using basis sets of split-valence quality. The electronic structure of the investigated systems is analyzed in terms of basis set effects, correlation effects, the role played by the transition metal, and the presence of non-transition metals.

Computational Details

Basis Sets. In the first basis set (hereafter called BS1) the s,p basis for nickel was taken from the (12s6p4d) set of ref 6 with the addition of two basis functions to describe the 4p orbital,[7] while the most diffuse s function was discarded. The Ni d basis was the reoptimized (5d) set of ref 8, contracted (4/1). This leads to an (11s8p5d) primitive basis for nickel, contracted (8s6p2d). The (6s4p) contraction of the primitive (12s9p) basis of McLean and Chandler[9] was used for magnesium, while the double-ζ expansion suggested by Dunning[10] was used for all the other ligand atoms, with a (4s/2s) basis for hydrogen and a (9s5p/4s2p) contraction for carbon, nitrogen, and oxygen.

The second basis set (hereafter called BS2) was derived from BS1 by adding 2p diffuse functions[11] to augment the basis set of nitrogen and oxygen, which present a consistent negative charge, as suggested by preliminary calculations performed with basis BS1.

In the MP2 calculations, effective core potentials (ECPs) were used. For nickel the argon core was described using the ECPs developed by Hay and Wadt.[12] The supplemented valence double-ζ basis set was employed.[12] For the first-row atoms, the 1s electrons were described using the ECPs reported in ref 13, while the valence shell was described using the supplemented valence double-ζ basis sets[13] with the addition of 2p diffuse functions on nitrogen and oxygen.[11] For hydrogen we used the same expansion as in the previously described basis sets. This basis set will be called hereafter BS3.

A slightly smaller basis set than BS3 was used in the calculations performed on the dimer. This basis set was derived from BS3 using a (4s/1s) contraction for hydrogen[14] and deleting the 2p diffuse functions on nitrogen and oxygen. This basis set will be called hereafter BS4.

Methods. Two levels of theory have been employed. Ab initio all-electron, spin-restricted Hartree–Fock gradient calculations were used in partial geometry optimizations of the ligands and in deriving estimates of the energy difference between the oxidized and reduced species for all the analyzed systems. Second-order Möller–Plesset calculations were subsequently performed on the nickel systems, using effective core potentials. Calibration calculations were performed by comparing all-electron and effective core potential results.

All computations were carried out by using the GAMESS[15] and HONDO[16] program packages, implemented on a IBM 3090 VEC computer.

Geometries and Geometry Optimization. The size of the real systems [Ni(salophen)] and $[\mathrm{Ni(salophen)ML}_n]_2$ is too large to allow a reasonably accurate ab initio investigation. It was necessary, therefore, to consider the simplified systems shown in Scheme IV, which should maintain the main features of the real [Ni(salophen)] complexes. The C–C bond which acts as the "electron reservoir" is a π bond in system II and a σ bond in system IV, both derived from an intramolecular reductive coupling. Most of the calculations have been performed on systems I–IV. However, also a dimer with an intermolecular C–C bond has been considered in order to approach closely the reduced form of the [Ni(salophen)] complex.[3]

The size of the investigated systems is too large to allow even a partial geometry optimization. The geometries of the analyzed complexes were deduced in this way: first of all, we performed a partial geometry optimization, using gradient techniques, of the systems reported in Scheme IV in the absence of the metal. We used then the results from these calculations, together with the experimental information of ref 3, to deduce the geometries reported in Figure 2. The geometry of the dimer, reported in Figure 1, was deduced from the geometries of systems I and II. The C–C bond length of the C–C bond which joins the two units was optimized by fitting the computed energy points to a second-order polynomial.

Results and Discussion

The total SCF energies of the systems under investigations, together with the energy differences Δ between oxidized and reduced species, are reported in Table I. Let us start our analysis from the systems in absence of the metal. Preliminary calculations have been performed on the systems I and II using basis set BS1. These calculations showed that the negative charge of the reduced species is mainly localized on the nitrogen and oxygen atoms, as it is shown by Table II, where we have reported the net atomic charges obtained by accumulating the Mulliken populations: this suggests the need for a better description of these atoms. Calculations performed with basis set BS2 confirm that the presence of diffuse functions on N and O is necessary to get a better description of the reduced species. For both basis sets, however, the energy difference between systems I and II is higher than 500 kcal·mol^{-1}, suggesting that system I does not have any

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(6) Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta* **1971**, *20*, 1.
(7) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1979**, *71*, 705.
(8) Rappe, A. K.; Smedley, T. A.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 2607.
(9) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
(10) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.
(11) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 4, p 1.
(12) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
(13) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.
(14) Van Duijneveldt, F. B. *IBM J. Res. Dev.* **1971**, 945.
(15) Guest, M. F.; Sherwood, P. GAMESS. SERC Daresbury Laboratory Report, 1990.
(16) Dupuis, M. HONDO. In *Modern Techniques in Computational Chemistry: MOTECC-89*; Clementi, E., Ed.; Escom: Leiden, the Netherlands, 1989.

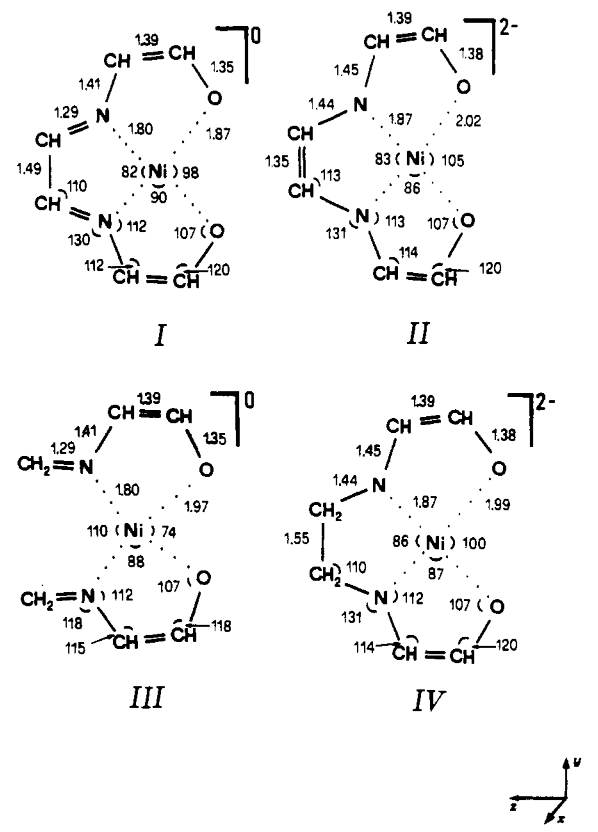


Figure 2. Geometries (in Å and deg) adopted for the model systems I–IV.

Table I. Total Energies (hartrees) and Energy Differences Δ (kcal·mol^{-1}) between Oxidized and Reduced Species for the Investigated Systems

method	I	II	Δ	III	IV	Δ
		No Metal				
SCF(BS1)	–488.8308	–487.9194	572			
SCF(BS2)	–488.8431	–487.9571	556	–489.9808	–489.0802	565
		M = Ni				
SCF(BS1)	–1995.6146	–1995.4871	80			
SCF(BS2)	–1995.6182	–1995.4995	74	–1996.7351	–1996.6512	53
SCF(BS3)	–125.8963	–125.7790	74	–127.0148	–126.9344	51
MP2(BS3)	–126.9259	–126.8322	59	–128.0569	–127.9895	42
SCF(BS4)	–125.8869	–125.7629	78			
SCF(BS4)		–251.7442[a]	19[b]			
		M = Mg				
SCF(BS2)	–688.7858	–688.6870	62	–689.9122	–689.8383	46

[a] Energy of the dimer species shown in Figure 1. [b] Difference between the energy of species I multiplied by two and the energy of the dimer.

tendency to be reduced. Moreover, this energy difference is so high that it cannot be substantially affected by correlation effects or by the stabilizing influence of a positive ion. System I, in the situation we are analyzing, cannot accept two electrons, and the reason is the destabilizing electrostatic interaction among the negative charges localized on the nitrogen and oxygen atoms, which are close enough to interact. For systems III and IV we have a comparable situation: the reduction implies a huge destabilization of the system.

Let us now consider the presence of a Ni^{2+} ion inside the cavity formed by nitrogen and oxygen atoms. The reductive process can lead in this case to the formation of a C–C bond or to a decrease in the oxidation state of the metal (as shown in Scheme V). We have performed, also in this case, preliminary calculations using basis set BS1. Once again, we noticed that the presence of diffuse functions on nitrogen and oxygen is necessary to get a better description of the systems. In particular, we can see from Table I that the energy of system I decreases by about 2 kcal·mol^{-1}, while that of system II decreases by about 8 kcal·mol^{-1}, using basis BS2 instead of BS1. From Table II, we can notice that the atomic charge on nickel in system I (+1.11 e) does not change upon reduction of the whole system, while the charges of all the other atoms decrease. In particular, the charge on nitrogen varies from –0.39 e to –0.82 e and that on oxygen from –0.61 e to –0.82 e. There is no change in the oxidation state of the transition metal, and the reduction process affects only the organic part of the system. The analysis of the molecular orbitals suggests that the Ni^{2+} is electrostatically bound to the nitrogen and oxygen atoms, which carry a consistent negative charge even in system I (see Table II), and it plays mainly a shielding effect among them. The Mulliken analysis shows that all the d orbitals of nickel, except d_{yz}, are doubly occupied. The d_{yz} orbital is almost unoccupied (0.47 e), and it is the main component of the lowest unoccupied molecular orbital (LUMO) localized on nickel. This orbital has its lobes pointing directly toward the negatively charged nitrogen and oxygen atoms: its occupation, therefore, would imply a huge increase in the Pauli repulsion and it is greatly disfavored. The two electrons we are adding to the system upon reduction prefer to localize on the ligand giving rise to a C–C π bond, at the expenses of two C–N π bonds. For systems III and IV we have a comparable situation, the main difference being that the "added" electrons give rise to a C–C σ bond.

From Table I we notice that the energy difference between systems I and II and that between III and IV are, respectively, 74 and 53 kcal·mol^{-1}. The reduction process requires in systems III and IV 21 kcal·mol^{-1} less than in systems I and II, and this difference is essentially due to the stronger σ bond formed in system IV, with respect to the π bond formed in system II. The Δ values for Table I for the nickel systems are smaller enough to suggest that, in the presence of a transition metal in the cavity formed by the ligand, the reduction process is possible, but it is not really isoenergetic.

All the results reported so far are at Hartree–Fock level. Correlation effects, however, should be relevant in our systems, where bond cleavage and bond formation are present. Correlation effects are surely important also for the description of the electronic distribution at the transition metal, but fortunately, they should be comparable in the oxidized and reduced species, since the metal plays essentially a "spectator" role in the reductive process. For these reasons, even a simple perturbative method as MP2 should be appropriate to obtain an estimate of the influence of correlation effects on the energetic balance of the reaction. Since the all-electron SCF calculations were very CPU-time consuming, we exploited the possibility to use ECPs to reduce the size of the problem. The SCF results obtained using the basis set BS3, which includes ECPs, compare very well with the BS2 all-electron results: in particular, the energy difference between systems I and II is essentially the same, while that between systems III and IV is lowered by only 2 kcal·mol^{-1} (see Table I). The MP2 results, reported in Table I, suggest that the correlation effects are more important for the reduced species than for the oxidized ones, as expected due to the larger number of electrons in the reduced form. They stabilize the reduced species more than the oxidized one: the energy difference between complexes I and II, indeed, decreases from 74 to 59 kcal·mol^{-1}, while that between systems III and IV is lowered from 51 to 42 kcal·mol^{-1}.

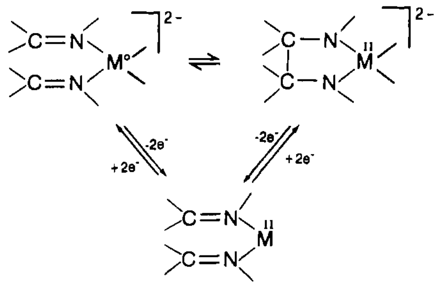
The use of ECPs allowed also the study of a more realistic model for the reduced species, i.e. the dimer reported in Figure 1. In order to make feasible the calculations, however, it was necessary to use a slightly smaller basis set, as we have explained in the computational details. From Table I, we can see that the energy difference between systems I and II, using BS4, is 78 kcal·mol^{-1}. This value should be compared to that obtained using BS1, which is 80 kcal·mol^{-1}, since both basis sets do not have 2p diffuse functions on N and O. The agreement between these values suggests that BS4 should provide reliable results. The difference between the energy of the dimer and that of species I multiplied by two is only 19 kcal·mol^{-1}, and this suggests that the dimer is a more realistic model for the reduced system than species II. This is essentially due to the fact that the negative

Table II. Net Atomic Charges (Electronic Units) Obtained by Accumulating the Mulliken Populations[a]

	M = Ni						M = Mg			
	I		II		III	IV	I	II	III	IV
M	+1.11	(+0.96)[b]	+1.11	(+1.00)	+1.09	+1.10	+1.75	+1.48	+1.71	+1.48
N	−0.39	(−0.34)	−0.82	(−0.69)	−0.36	−0.75	−0.62	−0.98	−0.59	−0.99
O	−0.61	(−0.62)	−0.82	(−0.75)	−0.60	−0.80	−0.74	−0.91	−0.67	−0.89
C_1[c]	−0.08	(−0.08)	−0.11	(−0.17)	−0.24	−0.13	−0.06	−0.06	−0.22	−0.12
C_2	−0.28	(−0.24)	−0.28	(−0.22)	−0.27	−0.16	−0.21	−0.11	−0.24	−0.08
C_3	+0.20	(+0.15)	+0.04	(−0.03)	+0.18	+0.04	+0.15	+0.02	+0.14	+0.02
H_1	+0.24	(+0.24)	+0.12	(+0.13)	+0.18	+0.08	+0.23	+0.11	+0.18	+0.09
H_2	+0.23	(+0.23)	+0.11	(+0.13)	+0.22	+0.11	+0.22	+0.10	+0.21	+0.10
H_3	+0.20	(+0.19)	+0.07	(+0.07)	+0.19	+0.07	+0.20	+0.07	+0.18	+0.07

[a] All-electron caculations performed with basis set BS2. [b] The values in parentheses use the BS1 basis set. [c] Symmetry nonequivalent carbon and hydrogen atoms as shown in Scheme IV.

Scheme V



charges in the dimer are more delocalized and this implies a reduction in the electronic repulsion. The optimized distance of the C–C bond which joins the two units was calculated to be 1.641 Å, in very good agreement with the experimental values reported for $[Ni(salophen)ML_n]_2$[3] and for sterically hindered residues joined by a C–C bond.[17] The Δ value we have obtained should be correct, taking into account the basis set incompleteness and the correlation effects. We can estimate the basis set error to be at least as high as 5 kcal·mol^{-1}, considering the effect of 2p diffuse functions on N and O, and the correlation around 10–15 kcal·mol^{-1}, as suggested by the MP2 calculations. Both these factors reduce the difference between oxidized and reduced species, suggesting that the reductive process is almost isoenergetic: the C–C bond formation and cleavage is essentially reversible, in agreement with the experiment.[3] This point suggests that solvation effects and solid-state forces are important but not essential in defining the energetics of the redox process.

The transition metal interacts only electrostatically with the ligand and does not participate directly to the reductive process: any other metal which does not change its oxidation state in the same situation should therefore promote the reductive process as efficiently as nickel. In this context, we decided to replace Ni^{2+} with Mg^{2+}, this choice being suggested by the presence of magnesium in chlorophyl, where reactions similar to those analyzed in this work should take place. From Table II, where we have reported the net atomic charges obtained by accumulating the Mulliken populations, we can see that the oxidation state of magnesium slightly decreases upon reduction: it is lowered by 0.27 e in systems I and II and by 0.23 e in systems III and IV. Most of the negative charge, however, is localized on the ligand in the reduced species: in particular, in system II (system IV) the charge on nitrogen is −0.98 e (−0.99 e), while that on oxygen is −0.91 e (−0.89 e). The oxidation state of magnesium does not change appreciably, and the "added" electrons upon reduction localize, as for the nickel systems, on a C–C bond far away from the metal. The results of Table I furthermore suggest that this process is almost reversible, the energy difference Δ being only 62 kcal·mol^{-1} in systems I and II and 46 kcal·mol^{-1} in systems III and IV. These values, moreover, should be reduced by considering a more realistic model system for the reduced species, i.e. a dimer.

The comparison with the energetics of the "real" redox process depicted in Scheme V should consider, however, other factors, which are impossible to include in such a kind of calculations. The chemical reduction of [Ni(salophen)][3] and [V(salophen)][4] occurs via a significant contribution derived from the binding of the alkali cations to the $O\frown O$ bite of the salophen and from their solvation. The chemical oxidation of the reduced form leads to the formation of new bonds, which can be a determining factor during the reaction.

Conclusions

The study at ab initio SCF and MP2 level of the model systems, reported in Scheme IV and Figure 1 and used for mimicking [Ni(salophen)] and its reductive product, has shown that Ni^{2+} does not change its oxidation state for the addition of two electrons to the system because no orbitals, localized on nickel and at low energy, are available to accept electrons, except the in plane d orbital, whose occupation would imply, however, a large increase in the Pauli repulsion. The "added" electrons prefer to form an additional C–C bond, which can be cleaved restoring the original product.

Ni^{2+} is electrostatically bonded to the ligand and acts as a shield among the negative charges of the ligand itself. This result suggests that any other M^{2+} ion, which under the same conditions does not change its oxidation state, could replace the nickel, and the calculations performed on the magnesium systems confirm this point. In case of magnesium the redox process of the ligand may have some behavior reminiscent of that of a chlorophillic-type ligand.

Correlation effects influence the energetic balance of the reductive process but not as heavily as expected for transition metal systems because the electronic distribution at the transition metal ion does not change in the reaction.

The theoretical calculations performed allowed us to get some fundamental information on molecules supported to be usable as "molecular batteries": (i) The electron addition to the complex occurs mainly on the ligand, and it does not affect very much the oxidation state of the metal. (ii) The metal is a spectator during the redox process, and a transition metal may be replaced by magnesium. (iii) The analysis of the energy difference between the electronic configuration of the oxidized and the reduced forms allows considerations on the reversibility of the process. The latest information can be used for understanding a qualitative energetic balance where to the weight of the electronic configuration we have to add the energy provided by the countercation bond formation and solvation in both oxidized and reduced forms.

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(17) Ahmed, F. R.; Neville, G. A. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2930.