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An electroanalytical investigation on the reduction of high-spin octahedral complexes of nickel(II) with Schiff base ligands

Salvatore Daniele
Department of Physical Chemistry, University of Venice, S. Marta 2137, 30123 Venice (Italy)
Mario Martelli
Department of Inorganic, Metallorganic and Analytical Chemistry, University of Padova, via Marzolo 1, 35131 Padua (Italy)
and **Gino Bontempelli**
Institute of Chemistry, University of Udine, viale Ungheria 43, 33100 Udine (Italy)

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Abstract

The electrochemical reduction of a series of high-spin octahedral complexes of nickel(II) with a variety of Schiff base ligands of the type R–N=CH–Py (Py = pyridyl; R = CH_3; C_6H_5; *o*-, *m*- or *p*-CH_3–C_6H_4; *o*-, *m*- or *p*-Cl–C_6H_4; *o*-, *m*- or *p*-CH_3O–C_6H_4) has been investigated in acetonitrile. All these complexes undergo a fairly reversible two-electron reduction process in which the parent hexacoordinate nickel(0) species is initially formed. This primary electrode product decomposes quickly in the homogeneous phase leading to the release of free ligands and to the formation of a tetracoordinate nickel(0) complex which is in turn of fairly low stability. The kinetic constant of the chemical decay following the charge transfer step has been determined for all the complexes investigated by the cyclic voltammetric approach. The dependence of the obtained kinetic constant values on the nature of the ligands present in the coordination shell is discussed together with the effect of these ligands on peak potential values. Also the circumstance under which all the nickel(II) complexes investigated are not reduced in steps to nickel(0) but undergo a direct two-electron uptake is considered by taking into account their high-spin configuration.

Introduction

The electrochemical reduction of both tetrahedral [1] and square-planar [2, 3] tetracoordinate nickel(II) complexes has been thoroughly studied in the last decade. This reaction turns out to occur, in any case, through two successive one-electron steps giving more or less stable nickel(I) and nickel(0) species. From this observation, selective and profitable electrochemical procedures, advantageous over chemical methods, have been proposed [4, 5] for generating *in situ* complexes of nickel in low oxidation states which are very attractive in view of their potential interest for technological applications to a variety of synthetic organic chemistry problems [6, 7].

Comparatively less attention has been devoted to the cathodic behaviour of octahedral nickel(II) complexes. In the cases investigated so far [3, 8, 9], however, these species have been found to be reduced directly to nickel(0) derivatives in a single two-electron step and no evidence for the formation of stable nickel(I) intermediates has been reported.

It is well known [10] that nickel complexes are species suitable for promoting in the homogeneous phase the synthesis of a series of organic compounds and that these metal-promoted processes occur in general through at least one redox step, involving the metal, in which one of the organic reagents is activated. Consequently, in view of the fact that electroanalytical methods offer the best approach for investigating reaction mechanisms involving redox processes, it appears convenient to gain further insight on the cathodic behaviour of octahedral nickel(II) species.

With this aim, we have carried out the present investigation concerning the electrochemical reduction of the octahedral complexes formed by nickel(II) with a series of Schiff base ligands of the type R–N=CH–Py (Py = pyridyl; R = CH_3; C_6H_5; *o*-Cl–C_6H_4; *m*-Cl–C_6H_4; *p*-Cl–C_6H_4; *o*-CH_3–C_6H_4; *m*-CH_3–C_6H_4; *p*-CH_3–C_6H_4; *o*-CH_3O–C_6H_4; *m*-CH_3O–C_6H_4; *p*-CH_3O–C_6H_4) which were deliberately synthesized. The synthesis and characterization of some

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of these nickel compounds have already been reported by other authors [11] who pointed out that they are high-spin complexes.

Experimental

Chemicals

All the chemicals used were of reagent grade quality. Reagent-grade acetonitrile was further purified as reported [12] and was stored over 0.4 nm molecular sieves under a nitrogen atmosphere. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was recrystallized from methanol and dried under vacuum at 50 °C.

N-Methylpicolinaldimine (CH_3–N=CH–Py) was synthesized by reacting an excess of methylamine, condensed into a flask at about −40 °C, with picolinaldehyde added dropwise. The obtained mixture was warmed slowly to room temperature under stirring and then dried by anhydrous Na_2SO_4, before distillation at 42 °C under reduced pressure (6 Torr). Other Schiff base ligands were prepared by the following general procedure. Picolinaldehyde and an equimolar amount of the appropriate amine (aniline or *o*-, *m*- or *p*-substituted aniline) were refluxed in ethanol for about 1 h. The solvent was then evaporated and the crude product was purified by recrystallization from benzene and petroleum ether.

The corresponding nickel(II) complexes were either prepared *in situ* by simple addition of three equivalent amounts of the desired free ligand to an acetonitrile solution containing a known amount of anhydrous nickel(II) perchlorate, or synthesized by mixing in methanol $NiCl_2 \cdot 6H_2O$ (2 mmol) with the appropriate Schiff base ligand (8 mmol) [11]. The addition to this last solution of KPF_6 (4 mmol) dissolved in water (30 ml) caused, upon cooling, the formation of dark orange crystals which were filtered off and washed with small amounts of ethanol–water mixtures. They were then recrystallized from acetone–ether solutions. Stock solutions of anhydrous nickel(II) perchlorate in acetonitrile were prepared by electrochemical oxidation of metallic nickel in TBAP–acetonitrile solutions at 0.5 V, as reported previously [13].

The elemental analysis data relative to both free ligands and the corresponding nickel(II) complexes are reported in Table 1.

Vis–UV spectra for these complexes in the solid state, obtained in KBr pellets, were coincident with those recorded in their acetonitrile solutions from 800 to 380 nm, where the solvent absorbance rose steeply, thus indicating that nickel(II) complexes retain in solution their octahedral configuration.

In all electroanalytical tests, fully deoxygenated nitrogen was used to remove dissolved oxygen from the working solution. This gas was first passed through sulfuric acid to remove traces of water and then equilibrated to the vapour pressure of acetonitrile.

Apparatus and procedure

Voltammetric experiments were carried out in a three-electrode cell. The working electrode was a glassy carbon or a platinum disc mirror-polished with graded alumina powder. In the cell, it was surrounded by a platinum spiral counter electrode. The potential of the working electrode was probed by a Luggin capillary reference electrode compartment whose position was made adjustable by mounting it on a syringe barrel. Moreover, in all measurements an *iR* compensation by a positive feedback was supplied.

Coulometric and preparative tests were carried out in a H-shaped cell with cathodic and anodic compartment separated by a sintered glass disc. A nickel spiral was used as the counter electrode, while the working electrode was a platinum gauze or a glassy carbon sheet.

In all cases, an aqueous SCE, connected to the cell by a salt bridge containing the medium employed also in the test solution, was used as the reference electrode.

The electroanalytical unit was a three-electrode system assembled with an Amel 552 potentiostat in conjunction with a function generator PAR 175 Universal Programmer and an Amel 731 digital integrator. The recording device was a Hewlett-Packard 7090 A measurement plotting system. UV–Vis spectra for nickel(II) complexes were obtained in both KBr pellets and acetonitrile solutions on a Perkin-Elmer model 575 spectrophotometer.

Unless otherwise stated, all the electroanalytical measurements were carried out at 25 °C in 0.1 M TBAP–acetonitrile solutions containing the investigated nickel complex at a typical concentration of 2.5×10^{-3} M.

Results and discussion

Preliminary voltammetric tests showed that the same results could be obtained whether the nickel complexes employed were chemically prepared or generated *in situ* upon addition of stoichiometric amounts of the desired Schiff base to solutions containing electrochemically generated nickel perchlorate. The second method was hence generally preferred because of its greater feasibility.

All the complexes investigated exhibited quite similar voltammetric profiles. Consequently, in order to illustrate the results obtained we discuss thoroughly

TABLE 1. Elemental analysis data

Compound[a]	C (%)		H (%)		N (%)	
	Calc.	Found	Calc.	Found	Calc.	Found
CH_3–N=CH–Py	69.97	69.69	6.71	6.84	23.31	23.16
$[NiL_3](PF_6)_2$	35.57	35.36	3.41	3.50	11.85	11.70
C_6H_5–N=CH–Py	79.10	78.83	5.53	5.61	15.37	15.21
$[NiL_3](PF_6)_2$	48.29	48.01	3.38	3.46	9.39	9.23
p-CH_3–C_6H_4–N=CH–Py	79.56	78.98	6.16	6.02	14.27	14.09
$[NiL_3](PF_6)_2$	49.97	49.24	3.87	3.80	8.97	8.74
o-$CH_3C_6H_4$–N=CH–Py	79.56	78.65	6.16	6.27	14.27	14.11
$[NiL_3](PF_6)_2$	49.97	49.29	3.87	3.89	8.97	8.76
m-CH_3–C_6H_4–N=CH–Py	79.56	78.31	6.16	6.05	14.27	14.15
$[NiL_3](PF_6)_2$	49.97	49.10	3.87	3.81	8.97	8.90
p-Cl–C_6H_4–N=CH–Py	66.52	66.11	4.19	4.33	12.93	12.72
$[NiL_3](PF_6)_2$	43.29	43.12	2.73	2.90	8.42	8.29
o-Cl–C_6H_4–N=CH–Py	66.52	65.83	4.19	4.27	12.93	12.68
$[NiL_3](PF_6)_2$	43.29	42.96	2.73	2.82	8.42	8.22
m-Cl–C_6H_4–N=CH–Py	66.52	66.10	4.19	4.35	12.93	12.70
$[NiL_3](PF_6)_2$	43.29	43.04	2.73	2.89	8.42	8.31
p-CH_3O–C_6H_4–N=CH–Py	73.57	72.86	5.70	5.91	13.20	13.03
$[NiL_3](PF_6)_2$	47.53	47.18	3.68	3.81	8.53	8.36
o-CH_3O–C_6H_4–N=CH–Py	73.57	72.92	5.70	5.87	13.20	12.96
$[NiL_3](PF_6)_2$	47.53	47.09	3.68	3.76	8.53	8.33
m-CH_3O–C_6H_4–N=CH–Py	73.57	72.78	5.70	5.94	13.20	12.89
$[NiL_3](PF_6)_2$	47.53	47.02	3.68	3.83	8.53	8.27

[a] In all nickel complexes L is the ligand listed above.

the cathodic behaviour of $[Ni(p\text{-}Cl{-}C_6H_4{-}N{=}CH{-}Py)_3]^{2+}$ which displays the cyclic voltammetric picture reported in Fig. 1. This Figure shows that in the cathodic sweep four peaks are recorded with which two anodic peaks are associated in the reverse scan.

The height of the very small pre-peak a turns out to increase linearly with the scan rate, thus suggesting that it is due to a surface limited process. This result agrees well with previous findings concerning aromatic diimine complexes [14] and can be accounted for by admitting that pre-peak a involves the same process operative also at peak b, but it is slightly shifted anodically thanks to the adsorption of the reduction product which is thus stabilized [15]. Its height is of course limited by the small aliquot of this product which undergoes adsorption.

Conversely, the linear increment of the height of the cathodic peak b observed with both the nickel complex concentration and the square root of the potential scan rate indicates clearly that the electrochemical process involved is diffusion controlled. Comparison of this height with that displayed under the same experimental conditions by the complex $[Ni(bipy)_3]^{2+}$ (bipy = bipyridyl), for which the occurrence of a two-electron reduction has been shown

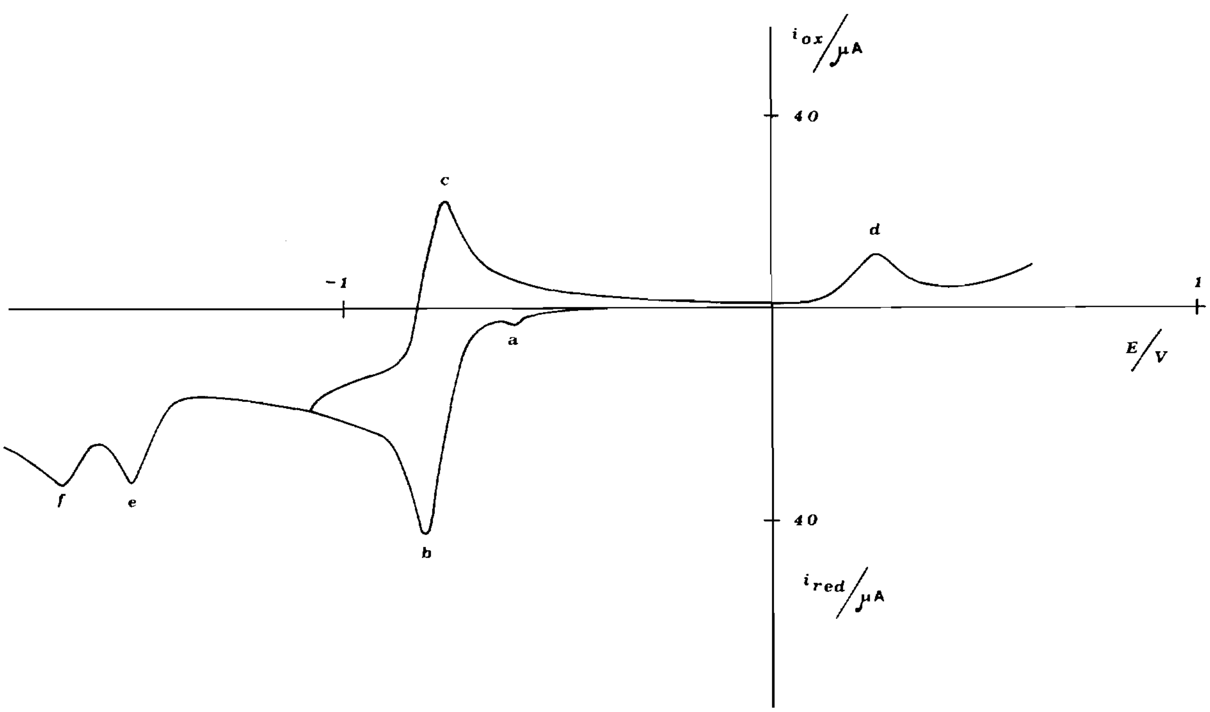

Fig. 1. Cyclic voltammogram recorded at 0.1 V s^{-1} with a glassy carbon electrode on a 0.1 M TBAP-acetonitrile solution containing 2.5×10^{-3} M $[Ni(p\text{-}Cl\text{-}C_6H_4\text{-}N{=}CH\text{-}Py)_3]^{2+}$.

unambiguously [9], points out that 2 mol of electrons per mole of nickel complex are required. This last conclusion is based on the reasonable assumption that the diffusion coefficients characterizing these fairly similar complexes do not differ appreciably.

Reduction peak b gives rise apparently, with oxidation peak c, to a cathodic–anodic system which turns out to involve a charge transfer appreciably reversible but followed by a chemical reaction leading to the decay of the primary reduction product. A satisfactory reversibility for the charge transfer is inferred by the fact that the peak potentials are practically unaffected by the potential sweep rate and that peak separation $E_{pc}-E_{pb}$ as well as peak width $E_{p/2}-E_p$ are equal to about 45 mV (theoretical 30 mV). From this fairly high reversibility, it can be stressed that no profound change both in geometric configuration and in the nature of the ligand set accompanies the charge transfer step [5].

The occurrence of the chemical reaction following the charge transfer becomes apparent by an increase of anodic peak c and a concomitant decrease of peak d until, at about 0.6 V s^{-1}, the peak ratio i_{pc}/i_{pb} attains unity whereas peak d disappears completely. A quite similar effect is produced by lowering the temperature from 25 to −25 °C. A progressive relative increase of peak c and a concomitant decrease of peak d are in fact observed until their heights become equal to that of peak b and nearly to zero, respectively, at −25 °C. These findings point out that the reduction product obtained at peak b, which is reoxidized at peak c, evolves quite rapidly to give a species oxidized at peak d.

Further insight on the chemical reaction leading to such a peak ‘conversion’ can be gained thanks to the presence in the voltammetric profile reported in Fig. 1 of peak f which is found to be due to the direct electrochemical reduction of free p-Cl–C_6H_4–N=CH–Py by comparison with the voltammetric behaviour of an acetonitrile solution containing this free ligand alone. When voltammograms are recorded on the corresponding nickel complex, the relative height of peak f decreases in fact with either increasing the scan rate or decreasing the temperature, until this peak vanishes (at *c.* 0.6 V s^{-1} or at − 25 °C, respectively) in concomitance with the disappearance of anodic peak d (see above). This result indicates unambiguously that also the free ligand is a product of the homogeneous reaction following the charge transfer step, like the species electroactive at peak d.

All these findings, together with the coincidence between UV–Vis spectra of nickel(II)complexes in the solid state and in acetonitrile solutions allowing the possibility of an extensive dissociation of the starting hexacoordinate nickel(II) species to be ruled out (see 'Experimental'), lead us to conclude that the electrochemical reduction process here considered occurs through the following EC pathway

$$[Ni^{II}(p\text{-}Cl\text{-}C_6H_4\text{-}N{=}CH\text{-}Py)_3]^{2+} + 2e^- \longrightarrow [Ni^0(p\text{-}Cl\text{-}C_6H_4\text{-}N{=}CH\text{-}Py)_3] \quad (1)$$

$$[Ni^0(p\text{-}Cl\text{-}C_6H_4\text{-}N{=}CH\text{-}Py)_3] \xrightarrow{k_f} [Ni^0(p\text{-}Cl\text{-}C_6H_4\text{-}N{=}CH\text{-}Py)_2] + p\text{-}Cl\text{-}C_6H_4\text{-}N{=}CH\text{-}Py \quad (2)$$

which resembles strictly that reported elsewhere for the electrochemical reduction of the quite similar nickel–bipyridyl complex [9]. This sequence shows that the nickel(II) complex undergoes the uptake of two electrons (peak b) yielding the parent nickel(0) species responsible for the associated anodic peak c. This electrode step is then followed by a fairly rapid decay of this nickel(0) species which leads in the homogeneous phase to the release of free ligand (reduced at peak f) and to the formation of a more stable tetracoordinate nickel(0) complex oxidized at peak d.

The occurrence of this EC pattern is fully confirmed by controlled potential electrolyses. Exhaustive reduction of the complex carried out at potentials corresponding to peak b requires in fact 2 mol of electrons per mole of nickel(II) initially present, while the solution turns from the initial orange to a dark blue colour which is usual for nickel(0) complexes with nitrogen-containing ligands [9, 16]. Voltammetric analysis of the electrolyzed solution shows the presence of peaks d and f alone and by controlled potential re-oxidation at peak d an orange solution is restored which exhibits the initial voltammetric profile (see Fig. 1). It must be noted, however, that only about 1.6 mol of electrons per mole of nickel initially present are required in this re-oxidation and that the height of all the restored cathodic peaks is lower than that expected for a quantitative regeneration of the starting nickel(II) solution. A possible explanation for this last finding can be advanced by admitting that nickel in the zero oxidation state undergoes in solution a fairly slow undesired reaction, uneffective in the voltammetric time scale, in which it is converted to a species no longer oxidized at peak d. In fact, similar nickel(0) complexes with ligands bearing a poor π-acceptor ability are known to be rather unstable in acetonitrile, probably because they undergo oxidative addition by the solvent to give cyanide–nickel derivatives [17] no longer electroactive in the accessible potential range. On the other hand, this expectation is substantiated by the fact that peak d, recorded after the reductive electrolysis at peak b,is found to decrease with time, even though slowly. Finally, it must be noted that the comparison of the height of peak f, monitored after completion of the mentioned reductive electrolysis, with a suitable calibration plot indicates the presence in the solution of an amount of released free ligand which agrees well with that expected on the basis of the reaction sequence reported above.

The results obtained in controlled potential electrolyses enable us also to ascribe cathodic peak e in Fig. 1 to the reduction of the ligand bound to the metal atom in the nickel(II) complex. This is strongly suggested by the fact that this peak is strictly related to peak b, in that it both decreases during reductive electrolyses at peak b and is restored after re-oxidation of the reduction product at peak d. On the other hand, an easier reduction for the ligand bound to the metal with respect to the free ligand must be considered reasonable in view of the electron-withdrawing effect which it is expected to undergo when accommodated in the coordination sphere of a nickel(II) ion.

All other complexes investigated exhibit the same cyclic voltammetric behaviour and lead to exactly the same findings by controlled potential electrolysis. Consequently, all conclusions drawn above can be extended to other species here considered. The corresponding peak potential values are collected and compared in Table 2.

Kinetic constants k_f, relative to chemical reaction (2) involving the release of the free ligand from the nickel(0) complex electrogenerated in the charge transfer (1), have been evaluated for all the complexes investigated by cyclic voltammetric measurements carried out by changing both the scan rate and the concentration of the electroactive nickel(II) complex. The ratio between the anodic current of peak c (i_{pc}) and the cathodic current relative to peak b (i_{pb}), measured at any scan rate, turns out to be practically unaffected by changes of nickel(II) concentration in the range 0.5–10 mM. This ratio falls within ±8% of an average value and no systematic trend is observed, thus allowing us to assign in any case a unity value to the kinetic order of chemical reaction (2). Consequently, the method suggested by Nicholson and Shain [18] for EC processes involving first-order irreversible chemical reactions following a reversible charge transfer has been applied. With this purpose, experimental i_{pc}/i_{pb} ratios measured at different scan rates (in the range 0.02–1.0 V s^{-1}) have been plotted against the logarithm of τ, i.e. the time spent in going from $E_{1/2}$ to the switching potential at which the scan direction is reversed. $E_{1/2}$ has been determined as the mean value between E_{pc} and E_{pb} [19] at a sufficiently high scan rate (1.0

TABLE 2. Data drawn from cyclic voltammetric experiments performed on a glassy carbon electrode at 25 °C. Peak potentials are recorded at 0.1 V s^{-1} and quoted vs. an aqueous SCE

Complex	Peak potential values (V)					k_f (s^{-1})[a]
	E_{pb}	E_{pc}	E_{pd}	E_{pe}	E_{pf}	
$[\mathrm{Ni(CH_3{-}N{=}CH{-}Py)_3}]^{2+}$	−1.10	−1.05	0.25	−1.85	−1.99	0.053 (±0.009)
$[\mathrm{Ni(C_6H_5{-}N{=}CH{-}Py)_3}]^{2+}$	−0.83	−0.79	0.50	−1.60	−1.73	0.078 (±0.008)
$[\mathrm{Ni}(p\text{-}\mathrm{CH_3{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.86	−0.81	0.35	−1.65	−1.77	0.070 (±0.011)
$[\mathrm{Ni}(o\text{-}\mathrm{CH_3{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.86	−0.81	0.34	−1.68	−1.80	0.066 (±0.014)
$[\mathrm{Ni}(m\text{-}\mathrm{CH_3{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.85	−0.80	0.31	−1.58	−1.73	0.072 (±0.011)
$[\mathrm{Ni}(p\text{-}\mathrm{Cl{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.80	−0.76	0.25	−1.48	−1.64	0.103 (±0.011)
$[\mathrm{Ni}(o\text{-}\mathrm{Cl{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.77	−0.73	0.26	−1.40	−1.58	0.098 (±0.012)
$[\mathrm{Ni}(m\text{-}\mathrm{Cl{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.78	−0.73	0.28	−1.42	−1.62	0.100 (±0.012)
$[\mathrm{Ni}(p\text{-}\mathrm{CH_3O{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.88	−0.83	0.36	−1.69	−1.82	0.092 (±0.009)
$[\mathrm{Ni}(o\text{-}\mathrm{CH_3O{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.90	−0.85	0.35	−1.71	−1.85	0.095 (±0.013)
$[\mathrm{Ni}(m\text{-}\mathrm{CH_3O{-}C_6H_4{-}N{=}CH{-}Py})_3]^{2+}$	−0.84	−0.79	0.38	−1.57	−1.75	0.094 (±0.011)

[a] Standard deviations in parentheses.

V s^{-1}) that the following chemical reaction is unable to affect voltammetric curves. The fit of the experimental plots obtained for the different complexes on the corresponding theoretical curves [18] allowed the relevant rate constants k_f to be estimated. Their values are reported in Table 2, last column.

Conclusions

The potentials corresponding to the reduction of the nickel(II) complexes investigated, reported in Table 2(E_{pb}), appear to depend on the nature of the Schiff base coordinated to the metal centre. The observed trend indicates in fact that this reduction becomes easier with the decreasing σ-donor ability of the ligand which is conditioned by the electron withdrawing effect exhibited by the organic group bound to the iminic nitrogen atom. This is proved by the fact that this sequence is in agreement with the facility to undergo electron uptake displayed by both free ligands (E_{pf}) and the same ligands bound to the metal (E_{pe}).

The quite high value observed in all cases for the kinetic constant k_f must be considered as the consequence of the well known reluctance of nickel(0) to be accommodated in an octahedral coordination sphere. The small differences found, even though fairly comparable with the experimental uncertainty, indicate that the stability of the primary nickel(0) species generated at the electrode surface increases slightly with the increasing electron withdrawing properties displayed by the *N*-imine substituent present in the ligand, in agreement with reasonable expectations. The products of such a chemical decay are in turn fairly low stable nickel(0) complexes and this fact makes the electrochemical route rather attractive for setting up synthetic processes of organic compounds promoted in the homogeneous phase by this type of nickel complexes. In fact, these processes frequently involve an oxidative addition of the organic substrate to the nickel atom in the zero oxidation state and this determining step becomes faster, of course, when ligands unable to give a complete stabilization of nickel(0) are employed [9]. This poor stability represents however a serious drawback for the preparation and recovery by the usual chemical procedures of these nickel promoters which are also hard to handle, but this difficulty can be easily overcome by taking advantage of the results reported above to electrogenerate *in situ* the desired nickel(0) species. Similar arguments also apply to synthetic processes in which the nickel(0) catalyst leads to the activation of the organic substrate by simple charge transfer [20], since the less stable nickel(0) species display of course the better reducing properties.

The circumstance under which all the nickel(II) complexes here considered undergo a two-electron reduction deserves a final comment. The uptake of two electrons in a single step is a reasonable consequence of the fact that the high-spin configuration of these species implies that the relevant spin-pairing energy is higher than the energy separation between the two highest orbitals, the latter being conditioned by a low field strength driven by 'hard' atoms such as nitrogen ones [21]. Thus, the transfer of the first electron from the electrode surface to the nickel(II) complex requires such an energy, as the result of the spin-pairing process involved, that it is sufficient to allow the second electron leading to a d^{10} configuration to be transferred as well. This statement is also substantiated by the fact that the octahedral low-spin nickel(II) complex $[\mathrm{Ni(bipy)_3}]^{2+}$ is only seemingly reduced to the corresponding nickel(0) species in a single two-electron cathodic process. As a matter of fact, this reduction turns out to occur conversely through two subsequent one-electron steps, even though they take place at quite close potential values [9, 22].

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