The Solution State of Nickel(II) and Nickel(I) in the Presence of Diphosphines in Acetonitrile. A Combined Electroanalytical and Spectrophotometric Approach

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Summary

The equilibria involving nickel(II), nickel(I) and nickel(0) in the presence of bidentate phosphine ligands in acetonitrile solution have been investigated by cyclic voltammetry, controlled-potential electrolysis, and spectrophotometry. The obtained results show that when both cone angles and P–P distance make the diphosphine well-suited to act as a chelating ligand, only bis-chelate complexes of the type NiL_2 are formed by nickel in all the three achieved oxidation states. Longer methylene chains interposed between the phosphorus atoms make the diphosphine less suited to act in a bidentate fashion, thus allowing lower-order complexes, e.g. $NiLS_2$ (S = solvent), to be obtained for nickel in the +2 and +1 oxidation states. Evidence for the poor stability of the $[Ni^I LS_2]^+$ complexes and for a higher-order complex of the type NiL_3 for nickel(II) have also been obtained. The dependence of the reduction potentials on the nature of the diphosphine employed is discussed.

Introduction

The influence of steric hindrance of coordinated phosphorus ligands on the reactivity of metal complexes is well recognized [1]. In particular, bond angle requirements in chelating diphosphines appear to affect remarkably the kinetic and thermodynamic stability of coordination compounds [1] and this effect matches with the 'anomalous' NMR chemical shifts [2] observed in the presence of such ligands. Thus, the reactivity of a transition metal in a low oxidation state towards oxidative addition reactions [1, 3], asymmetric induction [1], and other homogeneous catalytic processes [1] becomes considerably lower when in coordination sphere mono-dentate phosphine ligands are replaced by bidentate ones.

Electroanalytical techniques have been proved to be among the best procedures for investigating the stability and reactivity of coordination compounds which can undergo redox processes [4]. In particular, these methods have been successfully employed for collecting some important information on nickel complexes with monodentate phosphine ligands [5]. Consequently, we have adopted such an experimental approach in the study of the behaviour of nickel in the presence of 1,3-bis(diphenylphosphine)propane (dppp) and of 1,4-bis-(diethylphosphine)butane (depb) in order to investigate the role played by chelating diphosphines in determining the chemical and physico-chemical properties of the relevant metal complexes.

Experimental

Chemicals

All the chemicals employed were of reagent grade quality. Acetonitrile was further purified by distilling repeatedly from phosphorus pentoxide, and was stored on molecular sieves (3 Å) under nitrogen atmosphere. The supporting electrolytes tetrabutylammonium perchlorate (TBAP) and tetrafluoroborate (TBATFB) were prepared from tetrabutylammonium hydroxide and perchloric or tetrafluoroboric acid respectively. They were recrystallized from methanol and dried in a vacuum oven at 50 °C.

Stock solutions of anhydrous nickel(II) perchlorate in acetonitrile were prepared by anodic oxidation of metallic nickel in TBAP–acetonitrile solutions, as described in a previous paper [7]. All diphosphines were crystallized from methanol and stored in a vacuum oven. Nitrogen (99.99%), pre-

viously equilibrated to the vapour pressure of aceto-
nitrile, was used in the removal of dissolved oxygen.

Apparatus and Procedure

Voltammetric experiments were carried out in a
three-electrode cell. The working electrode was a
glassy-carbon disk surrounded by a Pt spiral counter-
electrode. The potential of the working electrode was
probed by a Luggin capillary reference electrode com-
partment, whose position was made adjustable by
mounting on a syringe barrel.

Coulometric and preparative tests were carried out
in an H-shaped cell with cathodic and anodic com-
partments separated by a sintered glass disk. The
working electrode was a platinum gauze and a mer-
cury pool was used as counter electrode. In all cases
an aqueous SCE was used as reference electrode.

The employed voltammetric unit was a three-
electrode system assembled with the MP-System 1000
equipment in conjunction with a in-house digital
logic function generator [6]. The recording device,
depending upon the scan rate employed, was either
a Hewlett-Packard 7040 A X–Y recorder or a Tracor
Northern NS-570 A Digital Storage Oscilloscope/
Waveform Digitizer with analogue output for X–Y
recorder.

In the controlled potential electrolyses an Amel
Model 552 potentiostat was used and the associated
coulometer was an Amel integrator Model 558. In
the spectrophotometric measurements a Perkin Elmer
576 spectrophotometer was employed.

All the electroanalytical measurements were made
at 25 °C, unless stated otherwise.

Results and Discussion

The voltammetric picture exhibited by electro-
generated nickel(II) perchlorate in acetonitrile is
reported in Fig. 1 (dashed line). As previously re-
ported [7], the species $[Ni(NCMe)_6]^{2+}$ is cathodically
reduced in an irreversible two-electron process to
metallic nickel, which can be re-oxidized to nickel(II)
in the associated anodic peak. The addition of the
employed diphosphines causes profound changes in
the observed voltammetric behaviour and these
changes are described in the following sections.

*Nickel–1,2-Bis(diphenylphosphine)ethane   (dppe)
System*

The electrochemical behaviour of nickel(II) in
the presence of the ligand $Ph_2P(CH_2)_2PPh_2$ has been
previously reported [5, 8] and is briefly summarized
here.

Such behaviour (see Fig. 1—full line) has been
rationalized on considering that for any ligand-to-
nickel ratio the only phosphine–nickel(II) complex
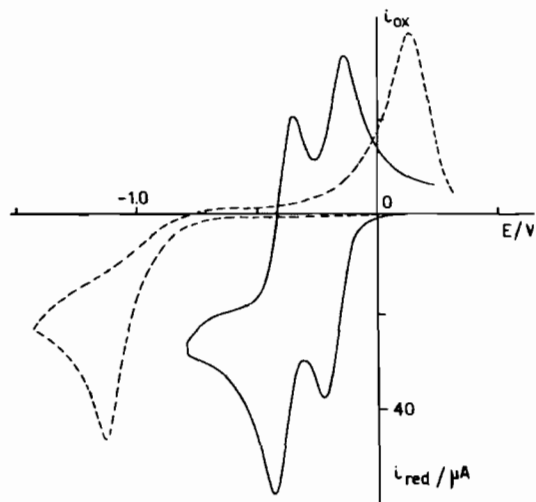which appears to be formed is $[Ni(dppe)_2]^{2+}$. This

Fig. 1. Cyclic voltammetric curves recorded with a glassy
carbon microelectrode on a CH_3CN solution containing Ni-
$(ClO_4)_2$ (5.0×10^{-3} mol dm^{-3}) and $[NBu_4][BF_4]$ (0.1 mol
dm^{-3}) (- - -); experimental conditions as above after addition
of dppe (0.01 mol dm^{-3}) (——). Scan rate 0.1 V s^{-1}.

complex is reducible in two one-electron and re-
markably reversible steps to give nickel(I) and
nickel(0) complexes respectively in which the coordi-
nation number does not change. On the contrary,
their geometric configuration changes gradually from
square-planar ($[Ni^{II}(dppe)_2]^{2+}$) to tetrahedral ($[Ni^0$-
$(dppe)_2]$), on passing through the 'square-planar–
tetrahedral' structure of $[Ni^I(dppe)_2]^+$. The relevant
potential values are reported in Table I.

*Nickel–1,3-Bis(diphenylphosphine)propane   (dppp)
System*

The voltammetric profile of $Ni(ClO_4)_2$ reported
with a dashed line in Fig. 1 becomes that reported
in Fig. 2-a when a dppp/Ni^{II} molar ratio equal to 1:1
has been attained. By increasing the amount of added
dppp, further changes can be observed, which are
illustrated in Fig. 2-b, 2-c and 2-d for convenient
values of the mentioned molar ratio.

The circumstance under which the height of the
observed peaks is conditioned by the ligand concen-
tration suggests the existence of more than one com-
plex for nickel in some of the involved oxidation
states. The nature of these complexes has therefore
been studied by employing both electroanalytical
and spectrophotometric measurements.

Electroanalytical Measurements

The maximum height for peak c_2 is reached at the
dppp/Ni^{II} molar ratio 1:1 and its comparison with
that relative to the first peak for $[Ni(dppe)_2]^{2+}$
(see the previous section) allows us to deduce that
in this peak a one-electron reduction process is also
operative. This process appears to involve an E.C.
sequence involving the species responsible for peak

TABLE I. Redox Potentials (V *vs.* aqueous SCE) Measured on a Glassy Carbon Electrode from Cyclic Voltammograms recorded at a Scan Rate of 0.1 V s⁻¹.

Redox process	L = dppe		L = dppp		L = depb	
	$E_{1/2}$[a]	ΔE_p[b]	$E_{1/2}$[a]	ΔE_p[b]	$E_{1/2}$[a]	ΔE_p[b]
$[Ni^{II}L_2]^{2+} + e^- \rightleftharpoons [Ni^IL_2]^+$	−0.25	0.06	0.17	0.08	−0.11	0.07
$[Ni^{II}LS_2]^{2+} + e^- \rightleftharpoons [Ni^ILS_2]^+$	−	−	−0.20	0.06	−0.37	0.08
$[Ni^{II}L_3]^{2+} + e^- \rightleftharpoons [Ni^IL_2]^+ + L$	−	−	−0.25[c]	irrev.	−	−
$[Ni^IL_2]^+ + e^- \rightleftharpoons [Ni^0L_2]$	−0.45	0.06	−0.49	0.06	−0.94	0.12
$[Ni^ILS_2]^+ + e^- \rightleftharpoons 1/2[Ni^0L_2] + 1/2Ni + 2S$	−	−	−0.84[c]	irrev.	−	−

[a]Determined as the mean value of $(E_p)_c$ and $(E_p)_a$ for the systems investigated. [b]$\Delta E_p = (E_p)_a - (E_p)_c$ gives an estimate of the reversibility degree for the redox system. [c]Peak potential.
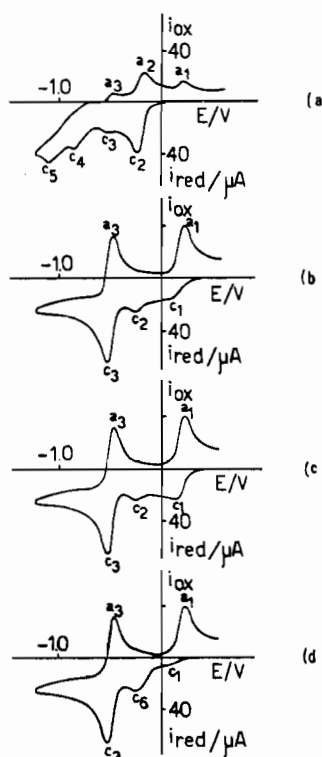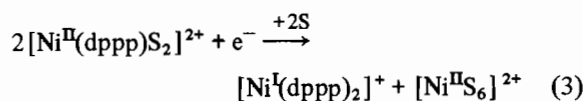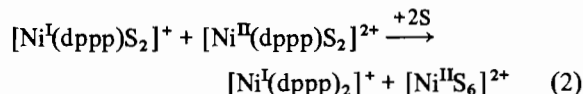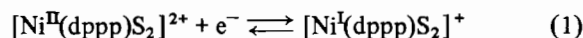

Fig. 2. Cyclic voltammetric curves recorded with a glassy carbon microelectrode on a CH₃CN solution containing Ni-(ClO₄)₂ (5.0 × 10⁻³ mol dm⁻³), [NBu₄][ClO₄] (0.1 mol dm⁻³) and dppp in the following molar ratios with respect to nickel(II): a) 1:1; b) 2:1; c) 4:1; d) 20:1. Scan rate 0.1 V s⁻¹.

a_2 as the product of the electrode step, and the depolarizer for peak a_1 as the product of the following chemical step. Cyclic voltammetric tests, carried out by increasing the scan rate and by lowering the temperature, show an increase of the ratio $(i_p)_{a_1}/(i_p)_{c_2}$ (which approaches unity) and a concomitant decrease to zero of the ratio $(i_p)_{a_1}/(i_p)_{c_2}$.

Controlled-potential electrolyses carried out at c_2 on nickel(II) solutions containing dppp in a molar ratio 1:1 gave an n_e value of 0.5, suggesting that half
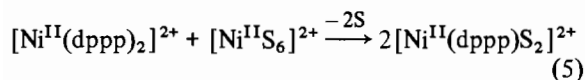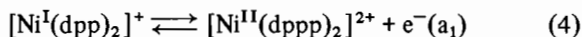
of the depolarizer is not reduced but is involved in the chemical step following the charge transfer. Only peaks a_1, c_3 and c_5 are voltammetrically detected in the electrolyzed solutions. Both in the oxidation at a_1 (which restores the voltammetric profile reported in Fig. 2-a) and in the reduction at c_3 (which gives the species responsible for a_3) was an n_e value of 0.5 found again, while in the reduction at c_5 (carried out after the reduction at c_3) 1 mol of electrons per mol of nickel(II) initially present are involved, giving metallic nickel as product.

The results obtained suggest that under the experimental conditions employed only one diphosphine molecule enters the coordination sphere of nickel(II). The species so obtained undergoes a one-electron process giving the parent nickel(I) complex, which does not reveal differences in geometry and composition as indicated by the reversible character of the redox system c_2–a_2. Apparently, this nickel(I) species (oxidizable at a_2) is not stabilized by the presence of only one diphosphine molecule in the coordination shell of the nickel atom, and it attains stability by coordinating an additional diphosphine ligand released from the nickel(II) complex which diffuses toward the electrode surface. In such a way, the species $[Ni^I(dppe)_2]^+$ (responsible for a_1) and $[Ni-(NCMe)_6]^{2+}$ (responsible for c_5—see Fig. 1) are detected after electrolysis, in agreement with the following reaction sequence (S = MeCN):

$$[Ni^{II}(dppp)S_2]^{2+} + e^- \rightleftharpoons [Ni^I(dppp)S_2]^+ \quad (1)$$

$$[Ni^I(dppp)S_2]^+ + [Ni^{II}(dppp)S_2]^{2+} \xrightarrow{+2S}$$
$$[Ni^I(dppp)_2]^+ + [Ni^{II}S_6]^{2+} \quad (2)$$

$$2[Ni^{II}(dppp)S_2]^{2+} + e^- \xrightarrow{+2S}$$
$$[Ni^I(dppp)_2]^+ + [Ni^{II}S_6]^{2+} \quad (3)$$

The above mentioned regeneration of the initial voltammetric profile observed after oxidation at a_1

has to be interpreted by considering that the charge transfer step is followed by the ligand-coproportionation reaction (5):

$$[Ni^I(dpp)_2]^+ \rightleftharpoons [Ni^{II}(dppp)_2]^{2+} + e^- (a_1) \qquad (4)$$

$$[Ni^{II}(dppp)_2]^{2+} + [Ni^{II}S_6]^{2+} \xrightarrow{-2S} 2[Ni^{II}(dppp)S_2]^{2+} \qquad (5)$$

As far as peaks c_3 and c_4 are concerned, our results suggest that they are due to the reduction to nickel-(0) of $[Ni^I(dppp)_2]^+$ and $[Ni^I(dppp)S_2]^+$ respectively. This assignment is based on the fact that both scan rate and temperature affect the relative heights of the peaks in the same way as they affect those of peaks a_1 and a_2 (due to the oxidation of the nickel(I) species). Moreover, peak c_4 (like a_2) is not voltammetrically detected after electrolysis at c_2 (thus indicating that the relevant depolarizer is an unstable species as it appears to be $[Ni^I(dppp)S_2]^+)$, while an n_e value of 0.5 is involved in the reduction at c_3 (like in the oxidation at a_1), as expected for the one-electron reduction of $[Ni^I(dppp)_2]^+$ formed from only half of the nickel initially present in solution (see reaction 3).
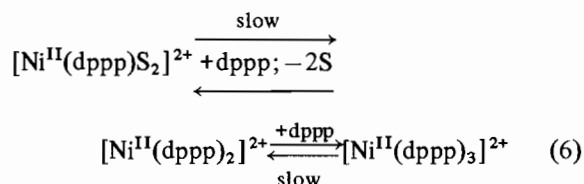
This analysis is also supported by the changes observed in the voltammetric profile when the dppp/Ni^{II} molar ratio is increased over 1:1. As shown in Fig. 2-b, when a molar ratio equal to 2:1 is attained both peaks c_4 and a_2 disappear in favour of c_3 and a_1 respectively. In addition, at this molar ratio an n_e value of one is involved in the electrolysis at c_3 and a_1, while peak c_5 is no longer detected. Under these experimental conditions, the diphosphine ligand now available in solution is evidently sufficient to allow the nickel(I) cathodically generated to gain stability by taking the form of $[Ni^I(dppp)_2]^+$, without subtracting the required ligand from the parent nickel(II) species (see reaction 2). In such a way, the depolarizer for peak $c_5([Ni^{II}S_6]^{2+})$ is not formed.

When the dppp/Ni^{II} molar ratio is increased over 1:1, peak c_2 decreases progressively while a new cathodic peak c_1 appears and increases at more positive potentials. The sigmoidal shape of peak c_1 (see Fig. 2-b) is progressively lost as this peak attains its maximum height (about one-electron, see Fig. 2-c) which is reached for a molar ratio *ca.* 5:1 when peak c_2 concomitantly disappears. By increasing the ligand-to-nickel ratio further, peak c_1 lowers and stresses once more its sigmoidal shape (see Fig. 2-d), while a new broad peak c_6 arises at potential values only a little more cathodic than those for c_2.

Voltammetric and chronoamperometric tests have indicated that the sigmoidal shape for peak c_1 is due to the occurrence of a C.E. process, *i.e.* the electrode step is preceded by a relatively slow chemical reaction in which the depolarizer is formed. A decrease in the ratio $i_p/v^{1/2}$ with increasing scan rates (0.03–50 V s^{-1})

and an increase with time in the value of $it^{1/2}$ has in fact been observed, as expected for such a process.

These findings clearly indicate that different ligand-to-metal ratios make possible the existence of at least three different nickel(II) complexes in slow equilibrium with one another. At low values of this ratio ($\leqslant$1:1) the complex $[Ni^{II}(dppp)S_2]^{2+}$ responsible for c_2 is the only species present; at higher ratios the depolarizer for c_1 is formed which is conceivably the complex $[Ni^{II}(dppp)_2]^{2+}$ in that when this peak reduces its kinetic character and reaches its maximum height (ratio *ca.* 5:1), it appears to be associated with a_1 (due to the oxidation of $[Ni^I-(dppp)_2]^+$—reaction 4) in an appreciably reversible cathodic–anodic system [4]. This fact implies that in the relevant redox process no appreciable change in the geometric configuration, as well as in the nature of the ligand set, is involved. Finally, for higher ratios ($>$5:1), a third diphosphine molecule enters the coordination sphere of nickel giving evidently the $[Ni^{II}(dppp)_3]^{2+}$ complex. A slow ligand dissociation equilibrium of this last complex can account for the kinetic character observed for c_1 at ligand to nickel molar ratios higher than 5:1 (see the right-hand side of scheme 6), while the kinetic behaviour exhibited by c_1 for lower molar ratios must be attributed to the slow association of dppp to $[Ni^{II}(dppp)-S_2]^{2+}$ (see the left-hand side of scheme 6):

$$[Ni^{II}(dppp)S_2]^{2+} + dppp; -2S \underset{\longleftarrow}{\overset{slow}{\longrightarrow}}$$

$$[Ni^{II}(dppp)_2]^{2+} \underset{slow}{\overset{+dppp}{\rightleftharpoons}} [Ni^{II}(dppp)_3]^{2+} \qquad (6)$$

This view is also confirmed by the results obtained by controlled coulometric experiments. One mol of electrons per mol of Ni^{II} is involved in the electrolyses carried out, for any ligand to nickel ratio $\geqslant$2:1, both at c_1 and directly at c_2 (or c_6 depending on the molar ratio employed) and in all cases the complex $[Ni^I(dppp)_2]^+$ as product is found. Moreover, after electrolyses at c_1, peak c_2 (or peak c_6) is no longer detected.

As for peak c_3, it involves a one-electron process when dppp/Ni^{II} ratios $\geqslant$2:1 are employed, giving in all cases the nickel(0) species responsible for the associated anodic peak a_3. The degree of reversibility exhibited by this cathodic–anodic system is in agreement with the occurrence of the following electrode reaction:

$$[Ni^I(dppp)_2]^+ + e^- \underset{(a_3)}{\overset{(c_3)}{\rightleftharpoons}} [Ni^0(dppp)_2] \qquad (7)$$
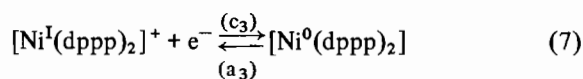
All the relevant potential values are reported in Table I.

Spectrophotometric Measurements

Spectrophotometric measurements carried out in parallel with the voltammetric ones on nickel(II) solutions containing increasing concentrations of added ligand show that only two absorption maxima (at about 315 nm and 425 nm) are detected for dppp/Ni^{II} molar ratios $\leqslant 1:1$. When higher ratios are employed, an intermediate absorption maximum at *ca.* 360 nm appears while for values higher than 5:1 both this absorption maximum and a new one developing at *ca.* 455 nm become more and more evident. Conversely, no absorption band is detected at wavelengths higher than 600 nm where tetrahedral nickel(II) complexes are expected to absorb [9].
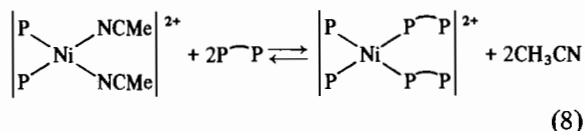
To obtain further information, the molar ratio method [10] as well as the continuous variation method [10] have been employed at different wavelengths in the region 310–550 nm. The relevant findings point out the existence of a 1:1 complex but do not allow a careful determination of stoichiometry of the higher-order complexes. To overcome this uncertainty, a set of curves relative to the continuous variation method has been simulated for a system consisting of an acceptor (Ni^{II}) able to give three successive complexes (NiL, NiL$_2$ and NiL$_3$, all characterized by absorption bands in the explored region) with the ligand L (=dppp).

Of course, the absorbance calculated for such a system depends both on the ϵ value of the three mentioned complexes at any λ employed* and on their stepwise stability constants K. By inserting roughly estimated values for these parameters in the equations suitable to describe the absorbance of the system, this last quantity can be calculated for any molar ratio. Following this procedure for a set of λ values, a set of simulated curves are obtained. Then, an iterative minimization of the differences between calculated and experimental absorbances makes possible the achievement of a satisfactory convergence which allows the determination of the following values for the stepwise stability constants: $K_1 \geqslant 2 \times 10^5$ l mol^{-1}; $K_2 = 3 \times 10^4$ l mol^{-1}; $K_3 = 2 \times 10^2$ l mol^{-1}.

To check the correctness of such a determination these parameters, together with the various ϵ values simultaneously determined, have been employed to reconstruct the mentioned spectra recorded for different dppp to nickel ratios, thus obtaining a fit whose accuracy is better than 5%.

In addition, the K and ϵ data obtained make it possible to infer the spectra referring to each nickel-(II) complex. These calculated spectra allow one to attribute an essentially planar geometry to all the three complexes. However, it is hard to admit that on

*Preliminary tests have proved that both the ion [Ni(NC-Me)$_6$]$^{2+}$ and the ligand dppp exhibit negligible absorbance at the wavelengths explored.

passing from NiL to NiL$_3$ only the following ligand exchange takes place:

$$\left|\begin{array}{c} P \\ \diagdown \\ P \end{array} Ni \begin{array}{c} NCMe \\ \diagup \\ NCMe \end{array}\right|^{2+} + 2P\frown P \rightleftharpoons \left|\begin{array}{c} P \\ \diagdown \\ P \end{array} Ni \begin{array}{c} P\frown P \\ \diagup \\ P\frown P \end{array}\right|^{2+} + 2CH_3CN$$

(8)

Such an exchange implies an increase of the ligand field effects and it should hence cause the absorption maximum to shift toward lower λ values, in contrast with the experimental finding. Therefore, if the ligand substitution reaction (8) is indeed operative, a fairly marked distortion toward the tetrahedral configuration has to be admitted. It must be remarked, however, that the mentioned shift of λ_{max} is also in agreement with a planar → trigonal bipyramid structural change. Consequently, the structure reported in Fig. 3 cannot be excluded for the NiL$_3$ complex.

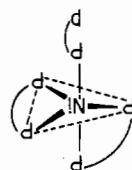Fig. 3. Hypothesis of a trigonal bipyramid structure for the [Ni(dppp)$_3$]$^{2+}$ complex.

Nickel(I) complexes responsible for peaks a$_1$ and a$_2$ (see Fig. 2) have been studied spectrophotometrically. To this purpose, near-infrared spectra have been recorded on dppp containing nickel(II) solutions after electrolyses both at c$_2$ and c$_1$. The obtained solutions (containing the depolarizer for peak a$_1$—see above) exhibit an absorption maximum located at 1200 nm ($\epsilon = 146$ l mol^{-1} cm^{-1}), as expected for the presence of a tetrahedral nickel(I) complex [5, 11, 12].

In the attempt to also record the spectrum exhibited by the unstable nickel(I) derivative responsible for peak a$_2$, controlled potential electrolyses at c$_2$ have been carried out at low temperature (−30 °C) on solutions containing nickel(II) and dppp at the molar ratio 1:1. Unfortunately, although the decay of such a nickel(I) species (see reaction 2) is remarkably slow at low temperature, it is again effective in the time-scale of the experiment. At −30 °C, it is possible however to record significant near-infrared spectra on the electrolyzed solutions containing both nickel(I) complexes which give rise to peaks a$_2$ and a$_1$, the decay of the low-stable species not being quantitative. An absorption band at 1200 nm is again observed, but it no longer exhibits symmetry characteristics, owing to partial overlap of the spectra due to the different nickel(I) species. By calculating the ratio between the absorbance read at 1400 nm (where this ratio is constant, thus pointing out that the

absorbing species is the stable [Ni(dppp)$_2$]$^+$ alone), it is possible to deduce the absorbance contribution due to the unstable complex at lower values (λ_{max} = 1050 nm).

The lower ligand field effect expected for the unstable [Ni^I(dppp)S$_2$]$^+$ complex with respect to the parent [Ni^I(dppp)$_2$]$^+$ does not agree with the higher energy required for the relevant d → d transition. This apparent disagreement can however be rationalized by admitting that the unstable nickel(I) complex is appreciably distorted toward the planar configuration. Such a statement is, on the other hand, in full agreement with the high degree of reversibility characterizing the cathodic—anodic system c_2—a_2, which points out that no appreciable structural change is involved in the relevant redox reaction. As nickel(II) is in fact apparently present in a planar arrangement, the parent nickel(I) complex is also expected to exhibit a rather similar configuration.

Nickel–R$_2$P(CH$_2$)$_4$PR$_2$ Systems

In the attempt of testing how the length of the methylene chain in chelating diphosphines affects the solution state of the related nickel complexes, some electroanalytical experiments have been carried out by employing 1,4-bis(diphenylphosphine)butane (dppb). Unfortunately, an extensive investigation in this case is precluded by the low solubility (ca. 10^{-3} mol dm^{-3}) both of the ligand and of the corresponding nickel(II) derivative.

On the contrary, reliable results can be obtained by using 1,4-bis(diethylphosphine)butane (depb) which is much more soluble in the employed medium. Nickel(II)—depb systems display a voltammetric profile which is dependent on the ligand-to-nickel molar ratio, as shown in Fig. 4 (related potentials are
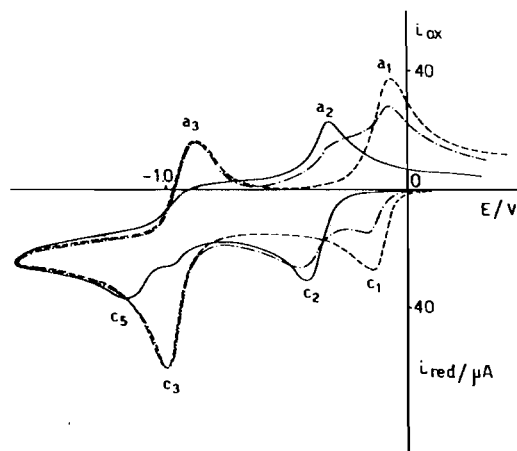

Fig. 4. Cyclic voltammetric curves recorded with a glassy carbon microelectrode in a CH$_3$CN solution containing Ni-(ClO$_4$)$_2$ (5.0 × 10^{-3} mol dm^{-3}), [NBu$_4$][ClO$_4$] (0.1 mol dm^{-3}) and depb in the following molar ratios with respect to nickel(II): (——) 1:1; (- - -) 2:1; (- - -) 30:1. Scan rate 0.1 V s^{-1}.

in the Table). These profiles closely resemble those exhibited by nickel(II) in the presence of dppp (see Fig. 2), except for peaks c_4 and c_6 which are not detected in this case. Moreover, such a strict analogy is confirmed by the results obtained in controlled potential coulometric experiments carried out at potential values corresponding to the various processes raised in evidence. Consequently, the conclusions previously drawn for the case of dppp can be transferred to this system, with the only exception of the absence of the [Ni^{II}L$_3$]$^{2+}$ species. The lack of peak c_6 indicates that the more basic ligand depb is surprisingly unable to give such a complex in contrast with the diphosphine dppp, thus suggesting that steric features rather than electronic ones play a decisive role in the stabilization of such a species.

As to the absence of peak c_4 (involving the reduction of the 'coordinatively unsaturated' nickel(I) species oxidizable at a_2), it can be reasonably explained on considering that the more basic character of depb causes in this case the occurrence of the related process at more negative potentials than c_5, i.e. when the response is no longer reliable owing to deposition of metallic nickel on the electrode surface.

Conclusions

Among the findings provided by this study, we wish to emphasize the dependence of the nature of the identified complexes, as well as of the relevant redox potentials, on the length of the methylene chain present in the employed diphosphines.

As to the nature of nickel(II) and nickel(I) species, our data do not give an unambiguous indication of the diphosphine coordination mode in NiL$_2$ complexes. In principle, these ligands can act either in a bidentate or in a monodentate fashion. Nevertheless, the quite high degree of reversibility characterizing both Ni^{II} → Ni^I and Ni^I → Ni^0 processes points out that no remarkable change in the chelating behaviour of the ligands accompanies the change of the metal oxidation state. Therefore, since all [Ni^{0}L$_2$] complexes appear to be bis-chelate in solution where they exhibit only a pale yellow colour [1], the same chelating coordination mode is conceivably expected also for the parent nickel(I) and nickel(II) derivatives.

On the other hand, on the basis of such a bis-chelate configuration the effect of the chain-length on the nature of the identified nickel(II) and nickel(I) complexes may be rationalized. When only two methylene groups are interposed between phosphorus atoms (dppe), both cone angles and the P–P length make the diphosphine well suited to act as a chelating ligand [1]; consequently, only a bis-chelate complex is formed by nickel in all the three achieved oxidation states. By increasing the length of the methylene chain (see dppp and depb) the chelating bite of the

ligands becomes less suited for a bidentate behaviour, thus allowing nickel(II) to give lower-order ([Ni-LS$_2$]$^{2+}$) or higher-order complexes ([NiL$_3$]$^{2+}$ in the case of dppp) in equilibrium with the bis-chelate [NiL$_2$]$^{2+}$, the stability not being so high as in the case of dppe. Of course, a smaller steric strain in these 'longer' diphosphines is expected when they act in a bidentate fashion on nickel(I) which is known to be larger than nickel(II). Consequently it is conceivable that [NiL$_3$]$^+$ species are not formed, while [NiLS$_2$]$^+$ is unstable. This poor stability must be related with the circumstance under which nickel(I) attains stability: only when ligands bearing a quite high π-acceptor ability (like phosphines) are present in its coordination sphere [5]. On the other hand, these arguments are substantiated by the observed existence for the diphosphines employed of a bis-chelate complex for nickel(0) which is even bulkier than nickel(I), and which requires the presence of the highest number of π-acceptor ligands in order to attain stability.

As far as the potential values reported in the Table are concerned, they are in an obvious correlation with the basicity of the employed diphosphine ligands [1]. These redox potentials appear however to depend also on the length of the methylene chain, although this dependence is not unequivocal. While nickel(I) becomes in fact increasingly difficult to reduce on increasing the chain-length, for the nickel(II) reduction such a sequence is not followed. A tentative explanation of this apparent disagreement can be given by considering the different steric strain which the diphosphine molecule undergoes when it is bonded in a chelating fashion to nickel in different oxidation states. Thus, in the nickel(II) reduction process both depolarizer and product are expected to be quite stable species (unstrained) in the presence of dppe, in contrast with the nickel(II) complexes formed with the other diphosphines which are less

prone to act as bidentate ligands. By taking into account the larger size of nickel in the +1 oxidation state, a 'release of strain' has to be expected in the $Ni^{II} \rightarrow Ni^{I}$ reduction in the presence of the longer diphosphines dppp and depb. Such a release of strain obviously affects the energetics of this redox process, thus making it easier to occur (as in the case of dppe). In other words, strain arguments make dppe almost uncomparable with other diphosphines. Of course, these differences in stability between the partners of the redox couple caused by strain effects are expected to be smaller in the $Ni^{I} \rightarrow Ni^{0}$ reduction in that the metal in these lower oxidation states has a larger size which allows all the employed diphosphines to act better as bidentate ligands.

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