The Electrochemical Behaviour of Mixed Nickel(II)-Chelates in Nonaqueous Solvents

Wolfgang Linert[a]; Ali Taha[a]; Reginald F. Jameson[b]

[a] Institute of Inorganic Chemistry. Technical University of Vienna, Vienna, Austria [b] Department of Chemistry, The University, Dundee, Scotland, UK

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THE ELECTROCHEMICAL BEHAVIOUR OF MIXED NICKEL(II)-CHELATES IN NONAQUEOUS SOLVENTS*

WOLFGANG LINERT,** ALI TAHA[⸸]

Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

and REGINALD F. JAMESON

*Department of Chemistry, The University, Dundee DD1 4HN, Scotland, UK*

The electrochemical reduction of solvatochromic and thermochromic mixed chelates of the type $Ni(\beta\text{-}dik)(diam)^+$, where β-dik represents a series of substituted β-diketonates and diam represents substituted diamines has been investigated at different temperatures in different solvents (DCE, An, Ac, DMF and DMSO). The observed polarographic two-electron reduction of Ni(II) on the Hg-electrode is irreversible in all solvents studied. Polarographic prewaves are observed which are interpreted in terms of kinetically and diffusion controlled electrode processes. $E_{1/2}$ is shifted to more negative potentials by increasing donor number (DN), decreasing temperature and the presence of electron-donating substituents. The temperature dependence of the Ni reduction potentials yielded two groups of solvents. This is interpreted as being due to different electrode kinetics involving diffusion and kinetically controlled rate-determining steps. The two groups further refer to a different stereochemistry of the solvated complexes in DCE, An and Ac on the one hand, and DMF and DMSO on the other. The results are discussed in terms of the extended donor–acceptor concept and related to results from UV, VIS and IR spectroscopy.

Keywords: Nickel, diketonates, diamines, electrochemistry, solvation

INTRODUCTION

Ni(II) chelates with a mixed coordination sphere consisting of a β-diketonate (β-dik⁻) and a diamine (diam) are known for their ability to coordinate donor solvent molecules. The associated equilibrium between a square planar, red and diamagnetic species $Ni(\beta\text{-}dik)(diam)^+$ and an octahedral, blue or green, paramagnetic $Ni(\beta\text{-}dik)(diam)(L)_2^+$ species provides the basis of solvatochromic and thermochromic properties of these complexes,[1−7]

$$Ni(\beta\text{-}dik)(diam)^+ + 2L \rightleftharpoons Ni(\beta\text{-}dik)(diam)(L)_2^+ \qquad (1)$$
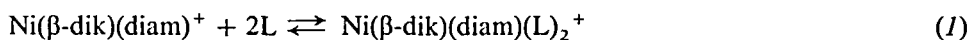
where L is the coordinating solvent molecule.

In a previous communication, a detailed investigation of equilibrium constants associated with this system has been reported.[8] In solvents with strong donor

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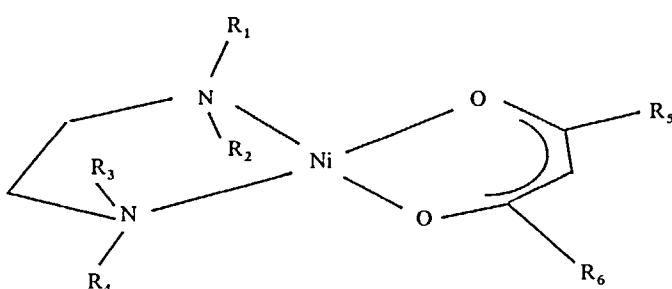
properties (for example DMSO or DMF) the octahedral complex is almost exclusively present whereas in weak coordinating solvents (for example in DCE or NE) only the square planar species is present. In a solvent of intermediate donor number (DN, alcohols, acetone *etc.*), both species coexist in comparable amounts so that the thermochromic behaviour, due to the exothermicity of the investigated reaction, becomes obvious.

The reduction of the Ni centre can be followed by polarographic means,[9] with varying temperature, in different solvents and with a series of substituents. For these investigations, the substituents at the diamine are positioned out of the ligand plane (*i.e.*, the plane formed by the square planar complex) so that substituents have been chosen based on their space filling properties in order to investigate steric influences. Substituents on the β-diketonate are expected to influence the π-electron system pointing to the importance of electron-withdrawing and electron-releasing effects of the substituents. Besides these aspects, the non-trivial electrode kinetics of the Ni(II)reduction[3] was a strong factor in encouraging us to perform such investigations.

TABLE I

Position of substituents in the ligands in the investigated mixed Ni(II) complexes.

Complex	R_1	R_2	R_3	R_4	R_5	R_6
Ni(acac)(tmen)BΦ_4	Me	Me	Me	Me	Me	Me
Ni(bzac)(tmen)BΦ_4	Me	Me	Me	Me	Me	Φ
Ni(dbm)(tmen)BΦ_4	Me	Me	Me	Me	Φ	Φ
Ni(tfac)(tmen)BΦ_4	Me	Me	Me	Me	Me	CF_3
Ni(dipm)(tmen)BΦ_4	Me	Me	Me	Me	t-Bu	t-Bu
Ni(acac)(Me$_3$en)BΦ_4	Me	Me	Me	H	Me	Me
Ni(acac)(teen)BΦ_4	Et	Et	Et	Et	Me	Me
Ni(acac)(Et$_3$en)BΦ_4	Et	Et	Et	H	Me	Me
Ni(acac)(dipe)BΦ_4	(CH$_2$)$_5$[a]		(CH$_2$)$_5$[a]		Me	Me
Ni(acac)(medach)BΦ_4	Me	(CH$_2$)$_5$[a]		H	Me	Me

[a] Bridging substituent.

EXPERIMENTAL

Chemicals were obtained from Merck and Rathburn Chemicals. Mixed B$\Phi_4{}^-$ complexes were prepared by the methods of Sone *et al.*[2] Solvents (1,2-dichloroethane (DCE), acetone (Ac), acetonitrile (An), *N,N*-dimethylformamide (DMF) and

dimethylsulfoxide (DMSO) have been purified according to standard procedures[10-11] or were of "spectral grade". The water content of the solvents used (except the ketones) was found to be below 30 mg dm^{-3} by Karl-Fischer titration. The polarographic measurements were performed as described earlier.[9] All measured half-wave potentials are quoted with respect to the reference bis(biphenyl)-chromium(I) tetraphenyloborate (BBCr).

RESULTS AND DISCUSSION

The reduction of the Ni centre of the investigated complexes can be followed by polarography at the dropping mercury electrode. A main reduction wave with a more or less pronounced prewave occurs in nearly all the investigated solvents. Cyclic voltammetry on the hanging Hg electrode shows that the main wave is irreversible and associated with a two-electron reduction in all observed solvents (Figs 1 and 2). The observed oxidation peaks refer to oxidation of the organic ligands.[9]
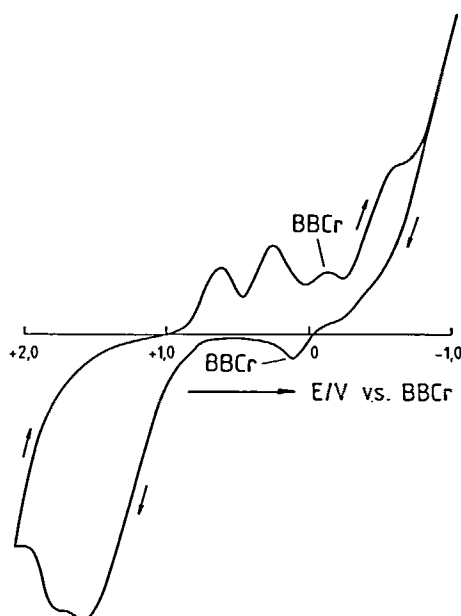
FIGURE 1 Cyclic voltammetry for 10 mM Ni(bzac)(tmen)BΦ_4 in DCE (0.1 M n-Bu$_4$NClO$_4$) at a hanging Hg drop electrode (scan rate 100 mV s^{-1}).

Logarithmic analysis (*i.e.*, log$\{i/(i_d-i)\}$ *versus* E) of the reduction waves (Table II) yielded two groups, one wth $\alpha n \leqslant 1$ and one with $\alpha n > 1$, approaching 2 in some cases. With an overall transfer of two electrons, the former group exhibits stronger irreversible behaviour than the latter.[12]

A titration of the square planar complexes with donor ligands such as DMF, DMSO *etc.*, shows that the peak current of the observed prewave is increased. The associated reduction potential is firstly shifted towards less negative potentials. After reaching a certain concentration, it starts to shift towards more negative potentials as
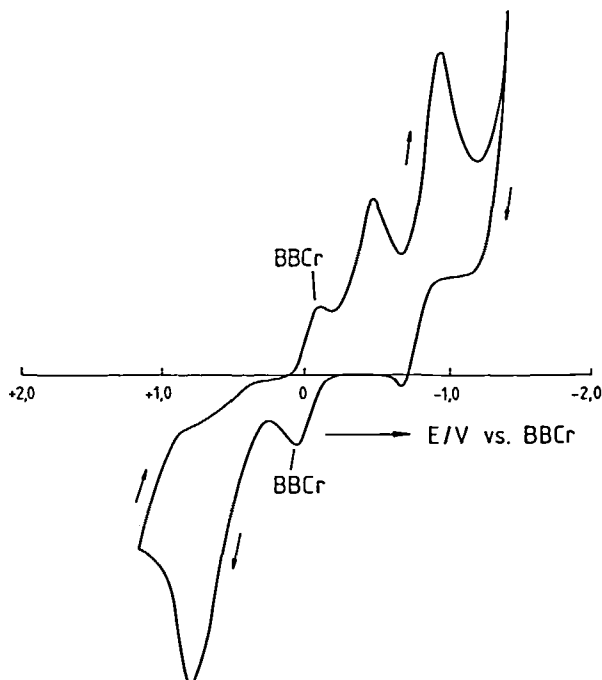
FIGURE 2   Cyclic voltammetry for 10 mM Ni(bzac)(tmen)BΦ_4 in DMSO (0.1 M n-Bu$_4$NClO$_4$) at a hanging Hg drop electrode (scan rate 200 mV s^{-1}).

TABLE II

Results from the logarithmic analysis: αn values for the complexes Ni(β-dik)(diam)BΦ_4 in different solvent at 25°C.

	DCE	An	Ac	DMF	DMSO
Ni(acac)(tmen)BΦ_4	1.75	0.96	1.83	1.09	0.83
Ni(bzac)(tmen)BΦ_4	1.36	2.00	0.87	1.26	0.81
Ni(dbm)(tmen)BΦ_4	1.18	0.93	1.17	1.39	0.98
Ni(tfac)(tmen)BΦ_4	1.28	0.97	0.93	1.00	1.06
Ni(dipm)(tmen)BΦ_4	1.07	1.05	0.88	1.00	1.01
Ni(acac)(Me$_3$en)BΦ_4	0.93	2.00	1.16	1.12	0.97
Ni(acac)(tecn)BΦ_4	1.32	1.80	1.08	1.36	0.88
Ni(acac)(Et$_3$en)BΦ_4	1.10	2.02	0.89	0.96	0.82
Ni(acac)(dipe)BΦ_4	0.90	1.79	0.89	1.18	0.89
Ni(acac)(medach)BΦ_4	0.92	1.01	1.42	0.95	0.86

expected from thermodynamic considerations (see Fig. 3). The former shift is commonly observed with Ni(II) complexes, for example when adding NH$_3$ or pyridine to aqueous solutions.[12,13] The shift to more positive values of half-wave potential, $E_{1/2}$, observed at low concentrations, can be explained by the existence of a kinetically controlled reaction in the electrode region. Depending upon the concentration ratio of the free ligand and the Ni complex, this reaction may or may not

produce a separate, visible shoulder or prewave on the polarographic wave. In cases of addition of An, Ac and acac only the first part of this curve (*i.e.*, the shift towards more positive potentials) is observed. Addition of diamine did not yield significant changes. This is in agreement with the observation that (contrary to β-diketone) octahedral complexes involving two diamine molecules are not formed.[2] The diamine appears not to take part in the electrode reaction (in distinction to the released β-diketonates).
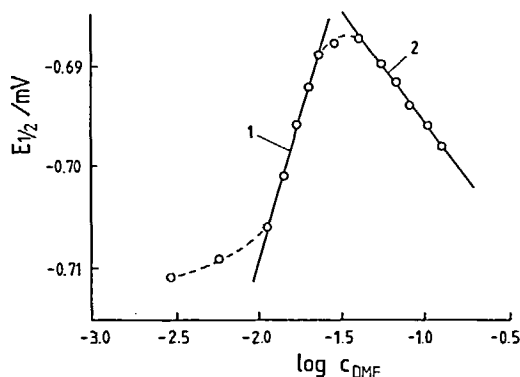

FIGURE 3   Dependence of half wave potentials ($E_{1/2}$) of the Ni(II)-reduction process ($E_{1/2}$) on the concentration of DMF for Ni(acac)(medach)BΦ_4 in DCE (0.1 M n-Bu$_4$NClO$_4$): 1 is the kinetically controlled part, 2 is the diffusion controlled part of the reaction.

The system appears similar to the Ni(II) reduction in aqueous systems in the presence of complexing agents[13] where the observed pre-wave refers to a kinetically controlled process and the main wave (occurring at more negative potentials) to a diffusion controlled process. The dependence of $E_{1/2}$ upon the ligand concentration [L] of an irreversible, but diffusion controlled electrode reaction of a system coordinating several ligand molecules, can be described[13] by (2).

$$\frac{dE_{1/2}}{d(\log[L])} = -(N-k)\frac{2.303\,RT}{\alpha nF} \tag{2}$$

In this equation N is the total number of solvating ligands possible (in our case $N_{max} = 2$, considering Ni(β-dik)(diam)$^+$ as being the species involved in further coordination), k is the number of ligands on the species directly reduced on the electrode, α is the transfer coefficient and n is the number of electrons transferred in the rate determining step); all other terms have their usual meaning. From αn (Table II), $N-k$ can be estimated.

In the case of kinetically controlled electrode reactions the dependence of $E_{1/2}$ on log[L] is given[13] by (3),

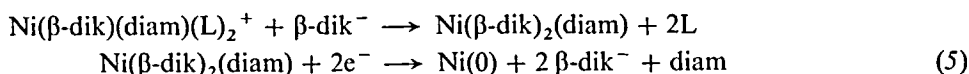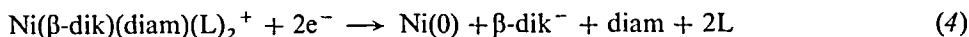$$\frac{dE_{1/2}}{d(\log[L])} = -(p-k-1/2)\frac{2.303\,RT}{\alpha nF} \tag{3}$$

where p is the number of ligands added without substitution ($p_{max} = 2$ yielding the octahedral complex species). The results of this analysis are given in Table 3.

TABLE III

Slopes (A) for the kinetic part $(p-k-1/2)$ and diffusion part $(N-k)$ of some mixed nickel (II) complexes with diketones and diamines.

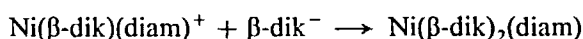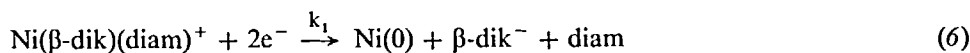| Complex	L	[L]/M	$\dfrac{dE_{1,2}}{d(\log[L])}$	A[a]	N[b]	p[c]	k[b,c]
Ni(acac)(medach)$^+$	An	0–4.85	0.17	2.6		0	2
	acac	0–0.11	0.079	1.26		2	1
	DMF	0–1.625	0.048	0.75		2	2
			0.019	0.30	2		2
Ni(bzac)(tmen)$^+$	An	0–3.35	0.06	1.89	2		0
Ni(tfac)(tmen)$^+$	An	0–0.425	0.029	0.63	1	0	

[a] $A = \alpha nFdE_{1,2}/2.303\,RTd(\log[L])$. [b] Estimated values with respect to diffusion controlled electrode reaction. [c] Estimated values with respect to kinetically controlled electrode reaction.
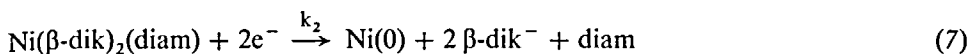
For strong donor solvents like DMF, DMSO and Py[13] both the kinetically and the diffusion controlled processes are accessible within the range of concentration during the titration procedure (see Fig. 3). For the kinetically controlled part (*i.e.*, at low donor solvent concentrations) we obtain $p-k=0$; this means that both p and k are most likely 2. For the diffusion controlled part of the curve (*i.e.*, higher L concentrations) the shift is towards more negative potentials; we obtain $N-k=0$, which means that both N and k are also most likely 2. The relatively high formation constants of the octahedral species suggest that these species are preferably present in solution. From this we conclude that, in strongly coordinating solvents, the reactions in the electrode environment are as follows

$$Ni(\beta\text{-dik})(diam)(L)_2{}^+ + 2e^- \longrightarrow Ni(0) + \beta\text{-dik}^- + diam + 2L \qquad (4)$$

$$Ni(\beta\text{-dik})(diam)(L)_2{}^+ + \beta\text{-dik}^- \longrightarrow Ni(\beta\text{-dik})_2(diam) + 2L$$
$$Ni(\beta\text{-dik})_2(diam) + 2e^- \longrightarrow Ni(0) + 2\,\beta\text{-dik}^- + diam \qquad (5)$$

In this the former represents the diffusion controlled step, whereas the latter step is the kinetically controlled one. This is further supported by titration of Ni(medach)(acac)$^+$ with acac as β-diketonate in DCE, where only the kinetically controlled step is obtained.
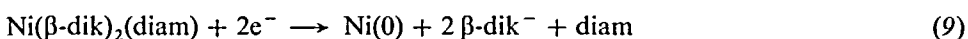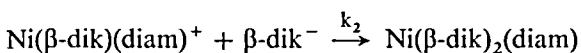
Three differently substituted Ni complexes were investigated in the less strongly coordinating solvents Ac and An, namely Ni(medach)(acac)$^+$, Ni(tmen)(bzac)$^+$, and Ni(tmen)(tfac)$^+$ given in the order of increasing formation constants for the octahedral complexes. In the case of Ni(medach)(acac)$^+$, even at large An concentrations, almost no octahedral Ni(medach)(acac)(An)$_2{}^+$ is present. The main electrode process is kinetically controlled (in this case no diffusion controlled step is observed) and we obtained $p-k=-2.10$, so that $p=0$ and $k=2$ appears to be most likely.

$$Ni(\beta\text{-dik})(diam)^+ + 2e^- \xrightarrow{k_1} Ni(0) + \beta\text{-dik}^- + diam \qquad (6)$$

$$Ni(\beta\text{-dik})(diam)^+ + \beta\text{-dik}^- \longrightarrow Ni(\beta\text{-dik})_2(diam)$$

$$Ni(\beta\text{-dik})_2(diam) + 2e^- \xrightarrow{k_2} Ni(0) + 2\,\beta\text{-dik}^- + diam \qquad (7)$$

The reduction process (6) yields free ligand resulting in the autocatalytic character of the prewave. Since in An and Ac the rate k_1 is much faster than k_2, the concentration of $Ni(\beta\text{-dik})(diam)^+$ is so low that (6) has minor importance. Hence reaction (7) is the rate-determining step which controls the reduction process in these solvents.

In the case of $Ni(tmen)(bzac)^+$ interacting with weakly coordinating solvents, the diffusion controlled region is reached, yielding $N = 2$ and $k = 0$. In An (unlike the case of DMF) the square planar complex predominates. This leads to a diffusion controlled step due to reduction of unsolvated square planar species.

$$Ni(\beta\text{-dik})(diam)^+ + 2e^- \xrightarrow{k_1} Ni(0) + \beta\text{-dik}^- + diam \qquad (8)$$

$$Ni(\beta\text{-dik})(diam)^+ + \beta\text{-dik}^- \xrightarrow{k_2} Ni(\beta\text{-dik})_2(diam)$$

$$Ni(\beta\text{-dik})_2(diam) + 2e^- \longrightarrow Ni(0) + 2\,\beta\text{-dik}^- + diam \qquad (9)$$
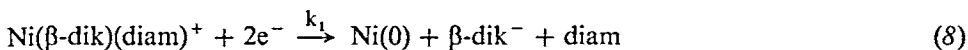
In this case, step (8) is the rate-determining step controlling the reduction process.

With some knowledge of the electrode reactions, the half-wave potentials of the main reduction wave can be investigated in some detail. The values *versus* the BBCr reference and their temperature dependence are given in Table IV.

The half-wave potentials ($E_{1/2}$) obtained for Ac and An solutions are more positive than that obtained with DCE since the rising part of the curve mentioned above (see Fig. 3) is not achievable even in pure An and Ac. On the other hand in pure DMF and DMSO more negative values are found since the solvation has gone further (*i.e.*, the rising part of the titration curve above is readily achieved).

The half-wave potential of the main reduction wave of $Ni(acac)(Me_3en)^+$, $Ni(acac)(Et_3en)^+$, $Ni(acac)(teen)^+$, $Ni(acac)(medach)^+$, $Ni(dipm)(tmen)^+$ and $Ni(acac)(dipe)^+$ become more negative in the sequence of solvents $An > Ac > DCE \gg DMSO \geq DMF$. For $Ni(bzac)(tmen)^+$, $Ni(dbm)(tmen)^+$ and $Ni(tfac)(tmen)^+$ $E_{1/2}$ values are found to become more negative in the order $DCE > Ac > An \gg DMF > DMSO$, whereas the simple complex $Ni(acac)(tmen)^+$, however, shows the sequence $Ac > An > DCE \gg DMF > DMSO$.

In general, increasing the donor number leads to more negative $E_{1/2}$ values for reduction. For the present systems this sequence is strictly obeyed for the complexes $Ni(bzac)(tmen)^+$, $Ni(dbm)(tmen)^+$ and $Ni(tfac)(tmen)^+$. A significant linear relation between DN and half-wave potential is found for $Ni(tfac)(tmen)^+$ (Fig. 4). The deviation of Ac can be attributed to steric hindrance of the alkyl groups and was also observed in previous spectrophotometric investigations.[8] For all other complexes, especially in weak donor solvents (DCE, An and Ac), the values of $E_{1/2}$ appear to be increasingly controlled by such steric factors, the influence of the donor–acceptor interactions being less pronounced.

Variation of substituents on the β-diketone ligand leads in the weak coordinating solvents DCE and Ac to more negative reduction potentials in the order $tfac > dbm > bzac > acac > dipm$. In An the sequence $tfac > dbm > bzac > dipm > acac$ is found. In the strongly coordinating solvents DMSO or DMF the observed half-wave potential becomes more negative in the order $bzac > acac > dbm > dipm > tfac$ or $dbm > bzac > acac > dipm > tfac$, respectively.

TABLE IV

Half wave potentials $E_{1/2}$ [mV] at 25°C of the diffusion wave of Ni(II) reduction in different solvents (0.1 M n-Bu$_4$NClO$_4$), their temperature dependent part $dE_{1/2}/dT$ [mV/K] and their temperature independent part $E_{1/2}$ (T = 0 K) [mV].

		DCE	An	Ac	DMF	DMSO
Ni(acac)(tmen)BΦ$_4$	$E_{1/2}$(298 K)	−620	−543	−527	−753	−734
	$dE_{1/2}/dt$	−1.95	1.90	2.53	0.77	1.12
	$E_{1/2}$ (0 K)	−27.1	−1120	−1260	−980	−1070
Ni(bzac)(tmen)BΦ$_4$	$E_{1/2}$(298 K)	−475	−492	−480	−712	−730
	$dE_{1/2}/dt$	−1.86	3.33	2.38	0.59	1.21
	$E_{1/2}$ (0 K)	82	−1490	−1190	−890	−1090
Ni(dbm)(tmen)BΦ$_4$	$E_{1/2}$(298 K)	−428.8	−487	−454	−686	−737
	$dE_{1/2}/dt$	−1.80	2.23	0.17	2.18	2.05
	$E_{1/2}$ (0 K)	−138.4	−1150	−502	−1335	−1348
Ni(tfac)(tmen)BΦ$_4$	$E_{1/2}$(298 K)	−165.0	−469	−389	−798	−825
	$dE_{1/2}/dt$	2.40	2.40	1.17	4.17	4.27
	$E_{1/2}$ (0 K)	−879	−1170	−740	−2040	−2100
Ni(dipm)(tmen)BΦ$_4$	$E_{1/2}$(298 K)	−656	−492	−532	−763	−786
	$dE_{1/2}/dt$	−0.29	1.79	0.79	0.42	0.88
	$E_{1/2}$ (0 K)	−501	−1130	−769	−888	−1050
Ni(acac)(Me$_3$en)BΦ$_4$	$E_{1/2}$(298 K)	−627	−546	−560	−816	−805
	$dE_{1/2}/dt$	0.388	3.76	2.26	0.86	1.84
	$E_{1/2}$ (0 K)	−685	−1670	−1235	−1070	−1360
Ni(acac)(teen)BΦ$_4$	$E_{1/2}$(298 K)	−596	−385	−486	−610	−632
	$dE_{1/2}/dt$	−1.65	2.95	1.02	2.64	2.24
	$E_{1/2}$ (0 K)	−62	−1260	−790	−1400	−1300
Ni(acac)(Et$_3$en)BΦ$_4$	$E_{1/2}$(298 K)	−630	−471	−530	−729	−715
	$dE_{1/2}/dt$	−0.66	3.65	1.54	2.78	1.75
	$E_{1/2}$ (0 K)	−391	−1560	989	−1560	1240
Ni(acac)(dipe)BΦ$_4$	$E_{1/2}$(298 K)	−535	−436	−464	−699	−652
	$dE_{1/2}/dt$	0.28	4.00	2.90	2.64	2.76
	$E_{1/2}$ (0 K)	−592	−1660	−1360	−1480	−1470
Ni(acac)(medach)BΦ$_4$	$E_{1/2}$(298 K)	−680	−419	−479	−687	−691
	$dE_{1/2}/dt$	−0.5	3.26	3.50	2.72	2.06
	$E_{1/2}$ (0 K)	−435	−1400	−1500	−1500	−1300

In general, electron-withdrawing and releasing effects such as those of the substituents R_5 and R_6 are described by the Hammett-parameter (σ) (Fig. 5). Linear dependence of $E_{1/2}$ and σ is indeed found and the temperature dependence shows isosubstituent relationships[16,17] (the appearance of two defined groups of solvents is discussed below). Dipe and medach (where no Hammett parameters are available) are not included, while for teen and Et$_3$en (where steric factors, which are not described by the Hammett parameter, appear to be crucial) the influences of R_1, R_2, R_3 and R_4 can be inserted into this relation. This underlines the additive character of Hammett's substituent parameters. The positive slopes of $E_{1/2}$ *versus* σ support the nucleophilic character of the electron-transfer reaction.[14] The substituent dependences decrease in general with increasing donor strength of the donor solvent present.
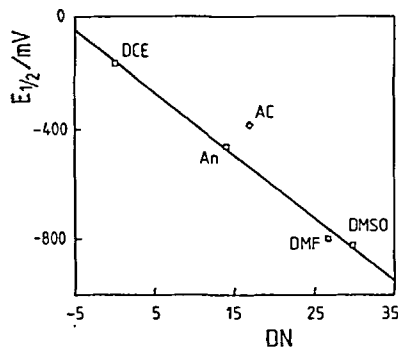
FIGURE 4 Half-wave potentials ($E_{1,2}$) of the Ni(II) reduction process (main wave) ($E_{1,2}$) *vs* the donor number (DN) for 0.001 M Ni(tfac)(tmen)BΦ_4 in DCE (0.1 M *n*-Bu$_4$NClO$_4$) at 25°C.
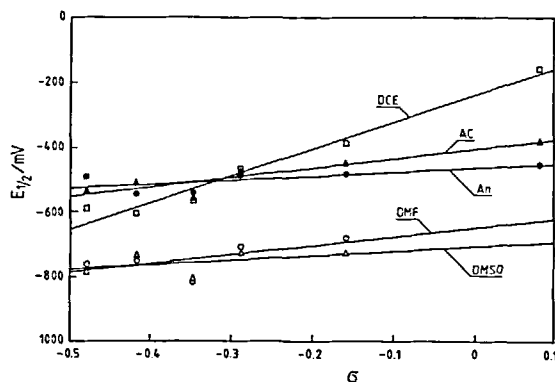

FIGURE 5 Half-wave potentials ($E_{1,2}$) of the Ni(II) reduction process (main wave) ($E_{1,2}$) *vs* the Hammett-parameter (σ) for 0.001 M Ni(β-dik)(diam)BΦ_4 in DCE (0.1 M *n*-Bu$_4$NClO$_4$) at 25°C.

The position of the IR absorption frequency associated with $v_{C=O}$ also yielded a linear relation with $E_{1/2}$ for all investigated solvents (Fig. 6). Increasing strength of the C=O bond in the sequence (*10*) is found (IR absorptions, $v_{C=O}$, of 1550, 1578, 1585, 1591 and 1606 cm^{-1} are measured in the solid tmen complexes with dipm, acac, bzac, dbm and tfac, respectively), correlating with increasing electron withdrawing properties of the substituents R_5 and R_6.

$$\text{dipm} < \text{acac} < \text{bzac} < \text{dbm} < \text{tfac} \qquad (10)$$

The same sequence is found for the Ni–O bond strength in the solid square planar complexes (v_{Ni-O} = 436, 437, 441, 440, 446 cm^{-1}, respectively). This agrees with the tendency of the square planar chelates to form octahedral species with donor molecules. As in the case of copper chelates[15] this sequence is associated with the order of increasing electron attracting properties of the β-diketonate as described by the Hammett parameter σ (dipm exhibits strong interligand repulsion). As shown in Fig. 7 the visible absorption band λ_2 (ascribed to a $^3T_{1g}(F)\leftarrow{}^3A_{2g}$ transition) is linearly dependent upon the reduction potentials, reflecting the associated ligand field strength.[8]
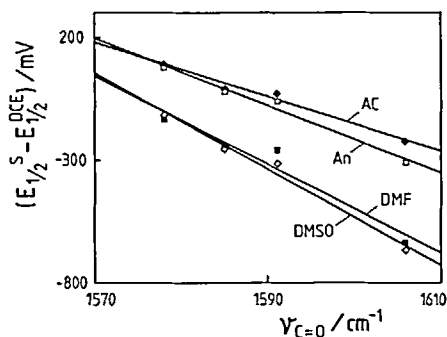
FIGURE 6   Half-wave potentials in different solvents ($E^S_{1/2}$) of the Ni(II) reduction process (main wave) with respect to the values in DCE vs the C=O stretching frequency ($v_{C=O}$) for 0.001 M Ni(β-dik)(diam)BΦ$_4$ in DCE (0.1 M n-Bu$_4$NClO$_4$) at 25°C.
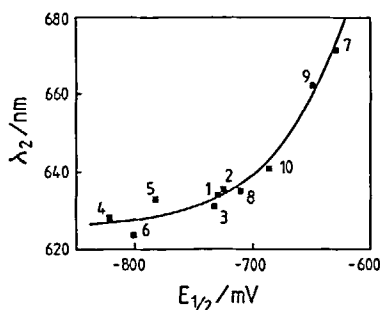

FIGURE 7   Position of the $^3T_{1g}(F)\leftarrow^3A_{2g}$ transition band (λ_2) vs $E_{1/2}$ for different Ni(β-dik)(diam)BΦ$_4$ complexes in DMSO.

When, on the other hand, the β-diketonate is kept constant (for instance acac) the half-wave potentials become more positive with the number and size of alkyl groups in the substituents R_1-R_4 on the diamine, yielding the following sequence in DCE: medach $\gg$ Et$_3$en > Me$_3$en > tmen > teen > dipe. This series can be divided into two groups, a symmetrical group: tmen > teen $\gg$ dipe, and an unsymmetrical group: medach $\gg$ Et$_3$en $\geq$ Me$_3$en. The order of the unsymmetrical group reflects changes in the ligand field strength of the diamines estimated from the values of λ_1 ($i.e.$, $^1A_{2g}\leftarrow^1A_{1g}$ or, in other words, $d_{x^2-y^2}\leftarrow d_{xy}$) of the square planar complexes in DCE.[8] The symmetrical ligand dipe appears to form less stable square planar complexes when compared with the tmen and teen complexes. Bulkiness and rigidity of the piperidine rings appears to hinder the formation of a chelate ring, and even when the chelate ring is formed, the bulky ligand will disturb the proper arrangement of other ligands and destabilize the whole complex. This explains the low reduction potential of Ni(acac)(dipe)$^+$ in DCE. In other solvents (An, Ac, DMF and DMSO) the observed half-wave potential becomes more negative in the order Me$_3$en > tmen > Et$_3$en > dipe > medach > teen. This is the order of decreasing steric hindrance on diamine ligands which controls the coordination of the solvent molecules.

The stability constants (log β) of different complexes coordinating two acetonitrile molecules yield linear relationships with $\Delta E_{1/2}$ (Fig. 8), reflecting the stability of the

octahedral complex formed; *i.e.*, increasing stability of the octahedral species leads to a more negative reduction potential.
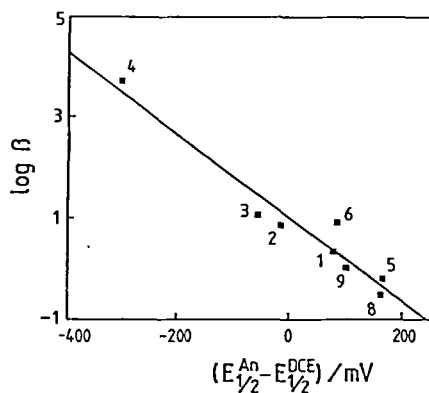

FIGURE 8 Formation constants, log β, *vs* half wave potentials measured in acetonitrile ($E^{An}_{1/2}$) of the Ni(II) reduction process (main wave) with respect to the values in DCE (0.1 M *n*-Bu$_4$NClO$_4$).
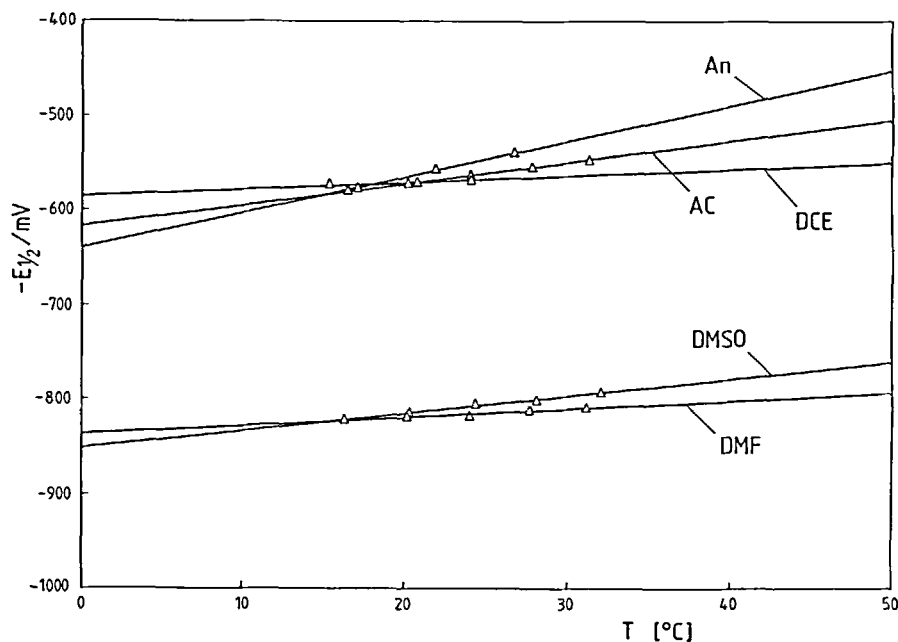

FIGURE 9 Temperature dependence of the half wave potentials for the Ni(II)-reduction process (main wave) of Ni(acac)(Me$_3$en)BΦ_4 in different solvents (0.1 M *n*-Bu$_4$NClO$_4$).

All Ni-complexes except Ni(tfac)(tmen)$^+$ in DCE show negative or very small positive temperature coefficients for the half-wave potentials (d$E_{1/2}$/dT), *i.e.*, increasing temperature leads to negative shifts in half-wave potential or only a small positive shift of $E_{1/2}$. In the case of Ni(tfac)(tmen)$^+$ the slope is large and positive, and is

associated with a destabilization of the square planar complex due to the electron attracting nature of the CF_3 group. In strongly coordinating solvents $dE_{1/2}/dT$ is positive (accompanied by thermochromic behaviour of these complexes and this behaviour is very similar to the spectroscopic results).[8] Figure 9 shows a typical example for the temperature dependence of the reduction potentials of $Ni(Me_3en)$ $(acac)^+$ in different solvents.

Highly statistically significant[16] isokinetic (isoequilibrium) behaviour (IKR) is found for all investigated complexes (Fig. 9), dividing the investigated solvents into two groups. The same grouping is found when investigating the substituent dependence (see above, Fig. 5) and the formation constants of five-coordinate and octa-hedrally coordinated derivatives of the square planar complexes.[8] The only exception in all these observations is $Ni(tmen)(tfac)^+$, which yields only one isokinetic or isoequilibrium group. It has been shown by theoretical and experimental investigations[17-19] that splitting into distinct IKR groups can be used as a tool for examining different reaction mechanisms. Accordingly, the present results confirm this, as one group includes the strong coordinating solvents, the other the weak or non-coordinating solvents; both exhibit different reaction mechanisms as pointed out above. The change from one group to the other is also reflected in the reaction mechanism for the formation of the octahedral species yielding, for example, *via* the trans configuration, an unchanged square planar arrangement of the diamine and β-diketonate ligands with the solvent donors DCE, An and Ac, whereas the diamine and β-diketonate ligands are twisted, allowing a cis addition of strong donor solvent molecules such as DMF, DMSO and Py.[8] Further investigation of this behaviour is continuing in our laboratories.

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