Solution Chemistry in Non-co-ordinating Solvents (CH_2Cl_2, $CHCl_3$) of Nickel(II) and Nickel(III) Complexes of the Lipophilic Macrocycle 1-Hexadecyl-1,4,8,11-tetra-azacyclotetradecane. The Emphasized Role of the Anion Co-ordination

Michela Di Casa, Luigi Fabbrizzi,* Mario Mariani, and Barbara Seghi
Dipartimento di Chimica Generale, Università di Pavia, viale Taramelli 12, 27100 Pavia, Italy

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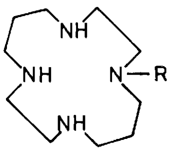
Nickel(II) complexes of the lipophilic tetramine macrocycle *N*-cetylcyclam (1-hexadecyl-1,4,8,11-tetra-azacyclotetradecane) L^1, dissolve in non-co-ordinating solvents such as CH_2Cl_2 and $CHCl_3$ as intact $Ni(L^1)X_2$ species, whose spin state and colour depend on the co-ordinating tendencies of the apically bound X^- anions: Cl^-, and SCN^-, blue, high-spin complexes; ClO_4^-, BF_4^-, and I^-, yellow, low-spin complexes. The complex $Ni(L^1)Br_2$ exists in solution as an equilibrium mixture of the blue and yellow species and the blue-to-yellow conversion is *exothermic*; moreover, the equilibrium is displaced to the right on further addition of the background electrolyte, tetra-alkylammonium or tetraethylphosphonium bromide. A general model is proposed to explain the thermodynamic aspects of the high-spin/low-spin interconversion in both co-ordinating (*e.g.* water) and non-co-ordinating media. Finally, $Ni^{II}(L^1)X_2$ complexes in CH_2Cl_2 solution (0.1 mol dm^{-3} $Bu^n{}_4NX$), undergo reversible one-electron oxidation processes to give a $[Ni^{III}(L^1)X_2]X$ species. The Ni^{III}–Ni^{II} redox potential decreases dramatically with increasing co-ordinating tendency of the X^- ions. This permits us to obtain a spectrochemical series for electrochemically inert inorganic anions. On this basis, it appears that ClO_4^- is a more strongly co-ordinating ligand than BF_4^-.

Fourteen-membered tetra-aza macrocycles (L), such as cyclam, (L^2), complex bivalent transition metal ions (Cr^{II}, Co^{II}, Ni^{II}, and Cu^{II}) to give species of formula MLX_2. *X*-Ray diffraction studies have shown that, in general, the metal centre is equatorially chelated by the macrocycle, with the axial sites co-ordinated by the inorganic anions X^-, giving rise to a more or less distorted *trans*-octahedral stereochemistry.[1] Of special interest is the case of nickel(II) complexes in which the type of anion determines the spin state of the metal centre. Co-ordinating anions (Cl^-, SCN^-, and N_3^-) stabilize the high-spin species (blue-violet colour), poorly co-ordinating anions (ClO_4^-, BF_4^-, and I^-) favour the formation of low-spin, yellow complexes.[2] However, when $NiLX_2$ complexes of the type described above are dissolved in a polar solvent (water, MeCN, or Me_2SO), the anion controlled discrimination of the spin state disappears owing to solvolysis and the metal spin state depends solely upon the donor properties of the solvent. In particular, nickel(II) cyclam complexes exist in solution as an equilibrium mixture of the blue, high-spin, and of the yellow, low-spin, forms.[3] The blue-to-yellow conversion, which is *endothermic*, is usually represented by equation (1), in which the yellow, square complex appears to originate from the release of two molecules of the solvent (solv) from the blue, octahedral species.

$$[NiL^2(solv)_2]^{2+} \rightleftharpoons [NiL^2]^{2+} + 2\ solv \qquad (1)$$

Moreover, in aqueous solution, further addition of the background electrolyte (*e.g.* NaX) favours the formation of the yellow form, independently of whether X^- is a non-co-ordinating (ClO_4^-) or a co-ordinating (Cl^-) anion.[4] Previous studies on the solution behaviour of nickel(II) complexes of cyclam and its analogues in water have suggested that the ions of the inert electrolyte compete for the solvent, thus reducing the number of molecules available for apical co-ordination to the metal centre.[5] More recently, detailed investigations on the effect of the background electrolyte on the high-spin/low-spin interconversion have been reported for the nickel(II) complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L^3), both in aqueous solution[6] and in non-aqueous media.[7] Also for the latter system, competition for the solvent molecules of the ions of the inert electrolyte has been suggested. Therefore, it appears that the solution chemistry of intact $NiLX_2$ species can only be investigated in absolutely non-co-ordinating media. However, this possibility seems precluded for the nickel tetramine complexes of the type discussed above due to their insolubility in apolar or weakly polar solvents.



$R = C_{16}H_{33}$ L^1
$R = H$ L^2

To circumvent this problem and so explore the anion controlled solution behaviour of nickel(II) tetramine complexes, we have prepared the novel tetra-aza macrocycle, *N*-cetylcyclam (1-hexadecyl-1,4,8,11-tetra-azacyclotetradecane), L^1 in which a lipophilic $C_{16}H_{33}$ chain has been appended, through a nitrogen atom, to the cyclam framework. Thus, corresponding $Ni(L^1)X_2$ complexes have been isolated, which in the solid state display the typical anion control of the spin multiplicity. Moreover, due to the presence of the lipophilic $C_{16}H_{33}$ chain, all the complexes, which are completely insoluble in water, dissolve in apolar or weakly polar solvents, such as CCl_4, $CHCl_3$, CH_2Cl_2, C_6H_6, *etc.* In the above media they are present as intact species $Ni(L^1)X_2$,

Table 1. Extraction of a NiX_2 salt from an aqueous solution (10^{-3} mol dm^{-3} in Ni^{2+} and 1 mol dm^{-3} in NaX) by an equal volume of CH_2Cl_2 (10^{-3} mol dm^{-3} in *N*-cetylcyclam)

X	Extraction yield/%*
F	18
Cl	44
Br	48
SCN	78
NO_3	43
ClO_4	59
BF_4	6

* Relative percentage of Ni^{2+} present in CH_2Cl_2 after the extraction to that present in the aqueous layer before extraction, calculated from the difference in the nickel content in the aqueous layer before and after extraction; ±2%.

and are high or low spin according to the nature of the X group. When X = Br or NO_3, in CH_2Cl_2 solution, the $Ni(L^1)X_2$ species exist as a mixture of the blue and yellow forms, the blue-to-yellow conversion being exothermic and influenced by the concentration of the background electrolyte MX (M = NR_4^+ or PR_4^+).

A further intriguing aspect of the solution chemistry of nickel(II) complexes with tetra-aza macrocycles in polar solvents is the easy access to the trivalent state, through one-electron anodic or chemical oxidation.[8] The relative thermodynamic stability of the nickel(III) tetra-aza macrocyclic complex, which is expressed by the magnitude of the Ni^{III}–Ni^{II} redox potential, is affected by the co-ordinating tendencies of the solvent, whose molecules can occupy the two axial sites of the distorted co-ordination octahedron.[9] Moreover, due to the strong affinity of the nickel(III) (low-spin) cation towards octahedral co-ordination, some inorganic anions (*e.g.* Cl^- or SO_4^{2-}) can compete for the axial position even in water, so exerting a remarkable stabilization effect.[10] In this work, an electrochemical investigation on the Ni^{II}–Ni^{III} oxidation process has been carried out in CH_2Cl_2 solution, in which any solvent binding effect can be ruled out. This enables the interpretation of the anion stabilization effect in the formation of trivalent nickel tetra-aza macrocyclic complexes.

Experimental

Materials.—The synthesis of *N*-cetylcyclam (L^1) has been described elsewhere.[11] $Ni(L^1)X_2$ Complexes were prepared by adding a hot butanolic solution of NiX_2 to a hot butanolic solution of L^1. On cooling, microcrystalline precipitates were obtained which were yellow (X = ClO_4^-, BF_4^-, or I^-) or blue-violet (X = Cl^-, Br^-, SCN^-, or NO_3^-). All the complexes satisfactorily analysed for C, H, and N. Tetra-alkylammonium salts were commercially obtained ($NBu^n{}_4BF_4$, $NBu^n{}_4ClO_4$, $NBu^n{}_4Br$, $NEt^n{}_4Br$, and $PBu^n{}_4Br$: Carlo Erba, analytical or polarographic grade) or prepared by reaction of the aqueous tetra-alkylammonium hydroxide with the appropriate acid, followed by recrystallization from diethyl ether–acetone.

Apparatus and Measurements.—Absorption spectra were measured by a Varian Cary 2300 spectrophotometer equipped with a thermostattable cell, using 1-cm quartz cuvettes. Atomic absorption spectra were carried out with an IL 501 apparatus. E.s.r. spectra, recorded at liquid nitrogen temperature, were measured with a Varian E-100 spectrometer, using diphenylpicrylhydrazyl (dpph) as a standard. Cyclic voltammetry experiments were carried out with an Electrochemolab Apparatus (Amel, Milan), using a three-electrode cell, thermostatted at 25 °C. The silver wire pseudo-reference electrode, was calibrated using ferrocene as an internal standard.

Results and Discussion

Nickel(II) N-*Cetylcyclam Complexes.*—Complexes of formula $Ni(L^1)X_2$ were obtained by reaction of *N*-cetylcyclam, (L^1), with the hydrated NiX_2 salt, in butanol and the microcrystalline solids recrystallized from CH_2Cl_2. The electronic properties of the complexes depend on the donor tendencies of the apically co-ordinated X^- anions. More strongly co-ordinating groups (Cl^-, Br^-, SCN^-, or NO_3^-) stabilize the triplet state (blue, paramagnetic complexes); less co-ordinating groups (ClO_4^-, BF_4^-, or I^-) stabilize the singlet state (yellow, diamagnetic complexes), in complete analogy with the corresponding complexes of the precursor ligand cyclam (L^2). All the complexes are soluble in CH_2Cl_2 and $CHCl_3$, whereas only the blue, high-spin salts are soluble in the apolar solvent CCl_4. Most of the complexes in solution retain their spin state, thus $Ni(L^1)Cl_2$ and $Ni(L^1)(SCN)_2$ display a three-band absorption spectrum in the *d–d* region, typically assigned to the high-spin 'octahedral' chromophore, whereas the yellow low-spin complexes show a single intense band centred at 475 nm (usually assigned to low-spin 'square-planar' complexes). In the investigated media, where solvent molecules cannot compete for co-ordination, axial sites of the co-ordination polyhedron are occupied by X^- anions. Chloride and thiocyanate ions bind the metal centre strongly enough to favour the high-spin electronic configuration, whereas perchlorate, tetrafluoroborate, or iodide ions do not exert axial interactions strong enough to stabilize the triplet state of the metal centre. In view of the extremely weak Ni^{II}–X interaction in these latter systems, the resulting low-spin complexes could be eventually described as ion pairs. In any case, solvent molecules are excluded from the apical sites and the stereochemical arrangement of the complexes can be described as a more or less distorted octahedron.

When $Ni(L^1)Br_2$ is dissolved in CH_2Cl_2 or in $CHCl_3$, mixed *d–d* spectra are observed, in which the absorption bands of both the blue and yellow chromophores are present (Figure 1), indicating that the high-spin and the low-spin complexes coexist in solution. Blue and yellow chromophores occur also on dissolution of $Ni(L^1)(NO_3)_2$ in $CHCl_3$ (but not in CH_2Cl_2 in which the high-spin state is retained). In general for anions of intermediate co-ordinating ability (Br^- or NO_3^-) a solvent dependence of the spin state is expected, with the high-spin state favoured by apolar solvents, *e.g.* CCl_4 in which the complex is exclusively in this form.

Solutions of $Ni(L^1)X_2$ complexes can also be prepared through extraction by L^1 of NiX_2 from an aqueous layer. According to this procedure, a layer of CH_2Cl_2, 10^{-3} mol dm^{-3} in L^1, is equilibrated with an equal volume of an aqueous solution of $NiSO_4$ (10^{-3} mol dm^{-3}) and NaX (1 mol dm^{-3}). The aqueous metal ion is extracted into the non-aqueous layer as a $Ni(L^1)X_2$ species, as indicated from the resulting absorption spectrum. The percentage transfer to the organic phase is measured by atomic absorption spectroscopy of Ni^{2+}(aq) both prior to, and subsequent to extraction. $NiSO_4$ has been chosen as metal source since independent experiments had shown that the $[Ni(L^1)]SO_4$ complex is not extracted at all into CH_2Cl_2. The amounts of the extracted metal for the various salts are reported in Table 1. It has been previously shown[12] that extraction of aqueous 3*d* metal ions by lipophilic tetramines is controlled by two main factors: (*i*) the hydration energy and (*ii*) the co-ordinating tendencies of the X^- anions: the less hydrated the anion and the stronger the Ni^{II}–X axial interactions, the higher is the extraction yield. Evaluation of the weight of the two independent contributions is not straightforward. From a

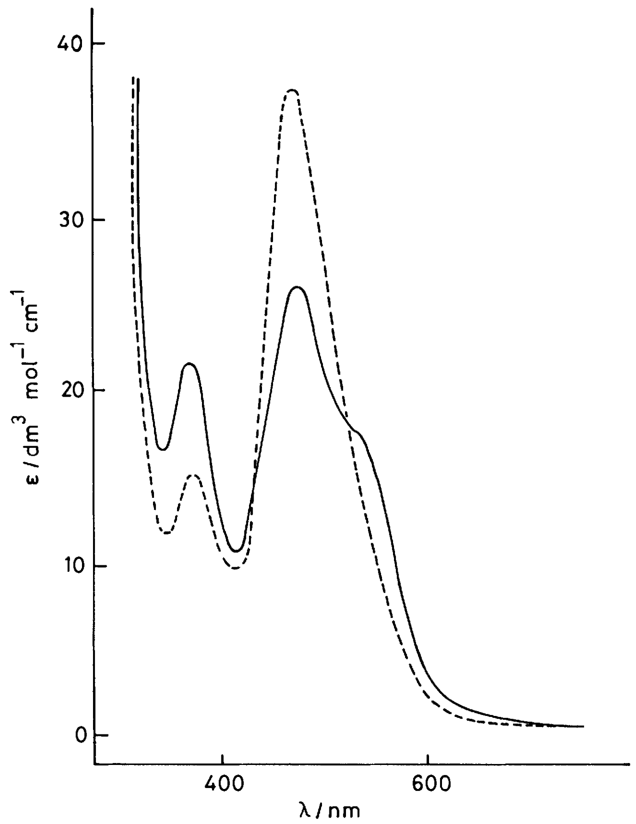


Figure 1. Absorption spectrum (solid line) of a 5×10^{-3} mol dm^{-3} CH_2Cl_2 solution of $Ni(L^1)Br_2$. The band at 365 nm and the shoulder at 560 nm originate from the blue, high-spin form. The band at 475 nm originates from the yellow, low-spin complex. The dashed curve refers to the same solution, which has been made 0.5 mol dm^{-3} in NEt_4Br, indicating a salting out effect on the yellow chromophore. Both spectra were taken at 25 °C

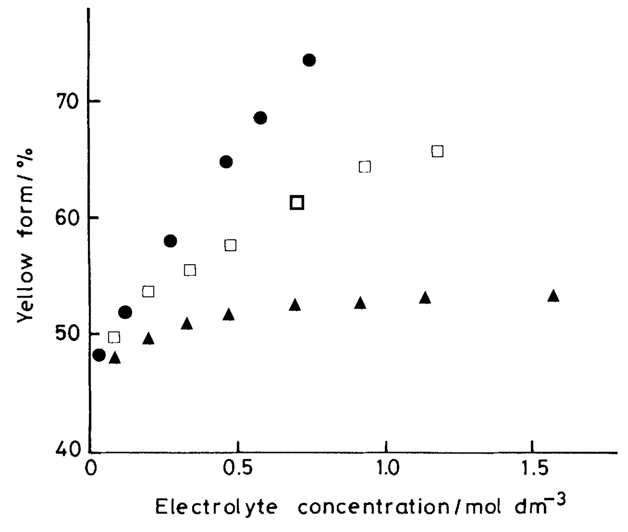


Figure 2. Effect of the concentration of the background electrolyte MBr [M = NEt_4 (●), $NBu^n{}_4$ (□), or $PBu^n{}_4$ (▲)] on the formation of the yellow, low-spin $[Ni(L^1)]Br_2$ complex in CH_2Cl_2 solution at 25 °C

very qualitative point of view, the relatively high extraction yield of the perchlorate salt (see Table 1) is probably a result of the low hydration energy of the anion, overshadowing its poor co-ordinating ability. On the other hand, the high extraction yield of the thiocyanate salt should result from the combined effects of both the low hydration enthalpy, as well as good ligating properties of SCN^-.

A further convenient method to generate the $Ni(L^1)X_2$ species in dichloromethane is based on the exchange of anions between the aqueous and non-aqueous layers. As an example, when a standard $Ni(L^1)(ClO_4)_2$ solution in CH_2Cl_2 (10^{-3} mol dm^{-3}) is equilibrated with an equal volume of an aqueous solution saturated in NaX the ClO_4^- ions are quantitatively replaced by X^- ions. It should be noted that all the three procedures are consistent, as quantitatively indicated by the resultant absorption spectra of the $Ni(L^1)X_2$ complexes.

Effect of the Background Electrolyte upon Spin-state Interconversion.—It has been anticipated that when the blue $Ni(L^1)Br_2$ complex is dissolved in CH_2Cl_2 or $CHCl_3$, a band centred at 475 nm, typical of the yellow, low-spin chromophore, appears in the *d–d* spectrum between the ν_2 and ν_3 bands of the blue species. Moreover, the intensity of the yellow band increases on addition of a bromide salt (*e.g.* NEt_4Br, see Figure 1) and decreases when the temperature increases. These observations are in accord with a blue-to-yellow interconversion equilibrium, which can be conventionally represented by equation (2).

$$\underset{\text{blue, high spin}}{[Ni(L^1)Br_2]} \rightleftharpoons \underset{\text{yellow, low spin}}{[Ni(L^1)]Br_2} \qquad (2)$$

In contrast to studies in aqueous solution or other co-ordinating media, the solvents here are not involved in the spin interconversion equilibrium.

In aqueous solution, the percentage of the yellow form and the equilibrium constant for the blue-to-yellow interconversion are conveniently determined through spectrophotometric investigations. Thus, $\%y = \varepsilon/\varepsilon_y$; $K = \varepsilon/(\varepsilon_y - \varepsilon)$, where ε represents the molar absorbance of the low-spin species at the equilibrium and ε_y is the limiting absorptivity of the yellow complex. Values of ε_y in aqueous solution can be obtained from spectra measured for a solution strongly concentrated in inert electrolyte (*e.g.* 7 mol dm^{-3} $NaClO_4$), where the complex exists totally in the low-spin form. A similar procedure cannot be employed to obtain the limiting absorbance values for the pure low-spin $[Ni(L^1)]Br_2$ in CH_2Cl_2 and $CHCl_3$; however, we have observed that, for complexes existing 100% as the yellow form, ε_y values do not depend on the type of anion: thus in CH_2Cl_2 for $[Ni(L^1)][ClO_4]_2$, $[Ni(L^1)][BF_4]_2$, and $[Ni(L^1)]I_2$ $\varepsilon_y = 58$ dm^3 mol^{-1} cm^{-1}. Therefore, it seems reasonable to assume that the bromide complex also should exhibit a comparable molar absorptivity value for the yellow form. Thus, taking a value of 58 dm^3 mol^{-1} cm^{-1} also for ε_y $\{[NiL]Br_2\}$, we calculate that the $NiLBr_2$ complex exists in CH_2Cl_2 at 25 °C as a mixture of 54% of the blue form and 46% of the yellow form.

Addition of background bromide salts MBr (M = NEt_4, $NBu^n{}_4$, or $PBu^n{}_4$) displaces the blue-to-yellow equilibrium (2) to the right. The effect is illustrated in Figure 2 and is especially evident with the tetraethylammonium salt, less pronounced with the tetrabutylammonium salt and for the tetrabutylphosphonium salt a saturation effect is achieved at low electrolyte concentration. This general behaviour is reminiscent of that observed in aqueous solution, where the blue-to-yellow equilibrium (1) is displaced to the right on addition of an inert salt (*e.g.* NaCl or $NaClO_4$) in which the ions of the inert salt are thought to remove solvent molecules thus favouring the formation of the yellow species.[3–5] An analogous mechanism cannot be proposed for CH_2Cl_2 solutions, where solvent molecules are definitively excluded from the co-ordination sphere. Moreover, it is worth noting that the salting out effect in CH_2Cl_2 is strictly related to the *type* of the tetra-alkyl cation

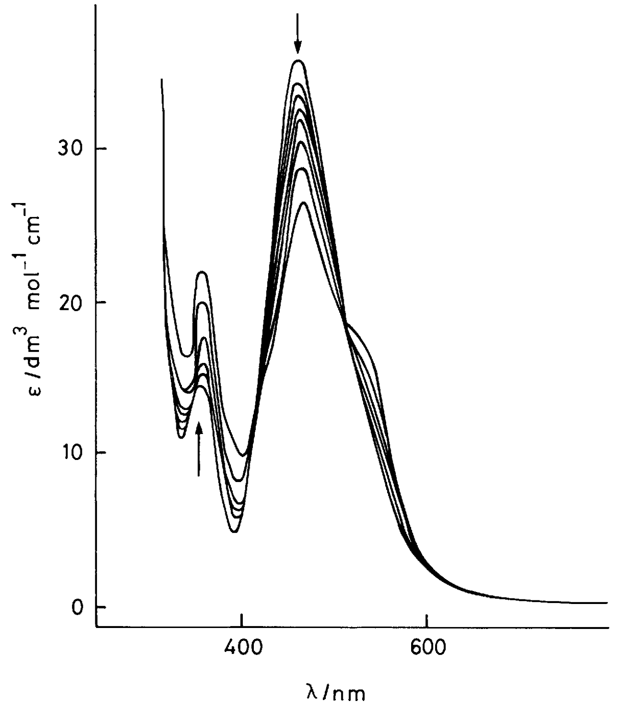


Figure 3. Temperature dependence of the *d–d* spectrum of the $Ni(L^1)Br_2$ complex in CH_2Cl_2 solution. A temperature increase makes the intensity of the band of the yellow species (λ = 475 nm) decrease, indicating that the blue-to-yellow conversion is exothermic ($\Delta H^{\ominus}$ = −6.3 kJ mol^{-1}). Spectra recorded at 5 °C intervals, from −25 to +25 °C. The concentration of the complex was 3.3×10^{-3} dm^{-3} mol

Table 2. Thermodynamic quantities at 25 °C associated with the interconversion equilibrium at 25 °C:

$$[Ni(L^1)X_2] \text{ (blue)} \rightleftharpoons [Ni(L^1)]X_2 \text{ (yellow)}$$

X	Solvent	Yellow form/%	log K^a	$\Delta H^{\ominus b}$	$\Delta S^{\ominus c}$
Br	CH_2Cl_2	46	−0.07	−6.3	22
Br	$CHCl_3$	64	0.26	−5.9	15
NO_3	$CHCl_3$	25	0.47	−3.8	22

[a] ±0.07. [b] kJ mol^{-1}; determined by linear least-squares analysis of log *K* *vs.* $1/T$ plot, ±0.5. [c] J K^{-1} mol^{-1}, ±2.

added and, in particular, it increases dramatically with the charge density of the 'onium' ion: $PBu^n{}_4{}^+ > NBu^n{}_4{}^+ > NEt_4{}^+$.

Effect of Temperature upon Spin-state Interconversion.—*d–d* Spectra in both CH_2Cl_2 and $CHCl_3$ vary markedly with temperature. In particular, increasing temperature results in an increase in intensity of bands due to the blue species and a decrease in that of the yellow form (Figure 3). This means that the blue-to-yellow conversion, described by equation (2), is *exothermic* whereas the same conversion in co-ordinating solvents (*e.g.* water or MeCN), represented by equation (1), is typically *endothermic*. Values for the equilibrium (2) have been determined over a range of temperatures (CH_2Cl_2, −25 to 25 °C; $CHCl_3$, −10 to 55 °C) and, through linear least-squares analysis of the Van't Hoff plots, $\Delta H^{\ominus}$ values have been obtained. These are reported in Table 2 with corresponding ΔS° quantities, calculated from $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ values, through the Gibbs–Helmholtz equation. The blue-to-yellow conversion shows comparable exothermic values for both CH_2Cl_2 and $CHCl_3$ solutions and is characterized by a negative entropy change.

The enthalpy change associated with equilibrium (2) can be split into two contributions: a term due to the variation of the ligand-field energy and a term which reflects the variation of the solute–solvent interaction energy, moving from the high-spin to the low-spin $Ni(L^1)Br_2$ species. Moreover, for speculative purposes, it is useful to split the ligand-field enthalpy term into two further contributions: (*i*) the variation of the equatorial bond energy (metal–macrocycle), defined as ΔH_{eq}, and (*ii*) variation of the axial bond energy (Ni–X), defined as ΔH_{ax} [equation (3)]. Moving from the blue, high-spin to the yellow,

$$\Delta H^{\ominus} = \Delta H_{eq} + \Delta H_{ax} + \Delta H_{solv} \qquad (3)$$

low-spin complex, the Ni^{II}–N bond length becomes much shorter (approximately from 2.1 to 1.9 Å, as judged from *X*-ray studies)[1] and the metal–nitrogen interaction is much more intense: thus, the H_{eq} term should be distinctly exothermic. On the other hand, ΔH_{ax} reflects the energy difference of the Ni–X axial interaction in the high-spin complex (very intense interaction) and in the low-spin complex (much weaker interaction). In particular, it is the ΔH_{ax} term that determines the spin state of a $Ni(L^1)X_2$ complex in a non-co-ordinating medium. In the presence of strongly co-ordinating anions (*e.g.* Cl^- or SCN^-) ΔH_{ax} overwhelms ΔH_{eq}, and the high-spin form $[Ni(L^1)X_2]$ is thus highly stabilized. Therefore, the insensitivity to any temperature increase for these blue complexes could be ascribed to the fact that the energy difference between the blue species and the much less stable yellow form is so large that it cannot be overcome through the temperature range typically allowed in solution. On the other hand, for very weakly co-ordinating anions, such as $ClO_4{}^-$, $BF_4{}^-$, and I^-, the equatorial term predominates over the axial contribution and the yellow, low-spin complex is the most stable form, and by a similar argument to that above, no yellow-blue interconversion is observed under the conditions studied.

However, some X^- anions of *intermediate* donating properties should exist, for which ΔH_{ax} and ΔH_{eq} quantities have comparable magnitude so that the enthalpies of the blue and yellow forms are not too different. Under these circumstances, changes in the relative proportions of the high- and low-spin systems should be observable under ambient conditions. In particular, the conversion will be endo- or exothermic depending on the relative positions of the two enthalpy levels. Such a situation seems to be present for the $Ni(L^1)Br_2$ complex. In this case, neglecting for a moment the solute–solvent contribution, the ΔH_{ax} term should be somewhat smaller than the ΔH_{eq} term, thus the energy level of the blue complex should be higher than that of the yellow form, making the blue-to-yellow conversion exothermic. On the other hand, an endothermic conversion should be observed in the presence of an axial group having co-ordinating tendencies moderately greater than bromide. This could be the case for water, if we were able to produce a *trans*-diaqua complex in CH_2Cl_2 or $CHCl_3$ solution. Direct comparison to aqueous solutions, where the blue-to-yellow conversion is *endothermic*, is however not valid due to the substantial difference in the solvation term of equation (3). Furthermore, the high-spin/low-spin conversion processes in CH_2Cl_2 and $CHCl_3$ are characterized by a *moderately negative* entropy change (which, for processes of the same type in aqueous solution, show a large *positive* entropy change). This behaviour can be ascribed to the fact that equation (2) does not involve any increase in the number of particles [as equation (1) does]. Moreover, it is possible that change from the high- to the low-spin form, which can be defined as more 'ionic' in nature, involves a relative increase of the solute–solvent interactions. This aggregation effect on the solvent molecules

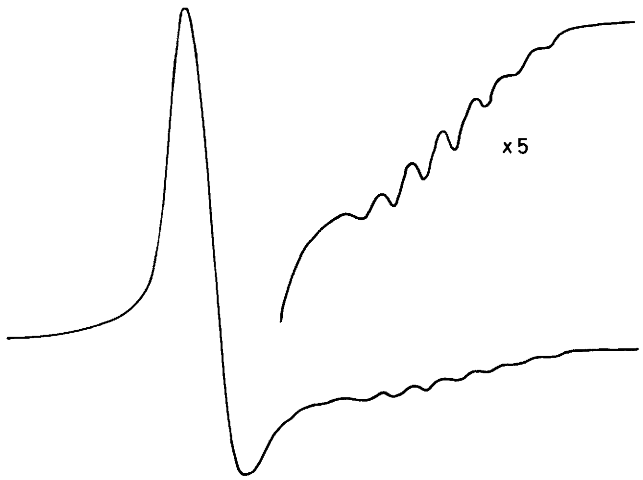


Figure 4. E.s.r. spectrum of a frozen solution (77 K) of $[Ni^{III}(L^1)Cl_2]Cl$ in CH_2Cl_2; $g_\perp = 2.18$; $g_\| = 2.03$

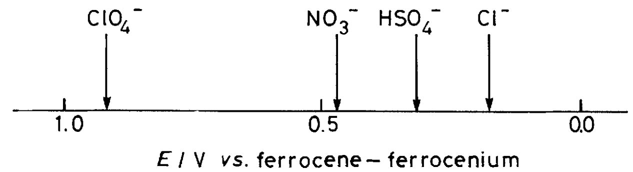


Figure 5. Potential diagram for the $[Ni^{III}(L^1)X_2]X + e^- \longrightarrow Ni^{II}(L^1)X_2 + X^-$ redox change in CH_2Cl_2 solution, 0.1 mol dm^{-3} in $NBu^n{}_4X$ at 25 °C

may contribute to the distinctly negative value of the entropy changes (see Table 2). However, it should be noted that a significant part of this negative contribution results from the reduction of the spin multiplicity associated with the blue-to-yellow conversion calculated to be -9.12 J K^{-1} mol^{-1} ($R \ln 1 - R \ln 3$).

Among the $Ni(L^1)X_2$ complexes investigated, we have found only one other that on dissolution generates a blue and yellow equilibrium mixture. This is the blue $Ni(L^1)(NO_3)_2$ complex, which in $CHCl_3$, at 25 °C, exists as 75% of the high-spin form and 25% of the low-spin form. Also in this case the blue-to-yellow conversion has been found to be exothermic and a ΔH° of -3.8 kJ mol^{-1} has been determined from spectrophotometric investigations at varying temperature. Following the previously outlined interpretational approach, one would attribute to the NO_3^- ion greater co-ordinating tendencies than to the Br^- ion, but not great enough to invert the sequence of the enthalpy levels of the high- and low-spin species, hence the blue-yellow conversion is exothermic.

The Ni^{III}–Ni^{II} *Redox Change.*—If dichlorine is bubbled through a CH_2Cl_2 solution of $Ni(L^1)Cl_2$ the blue-violet solution turns bright yellow, indicating the formation of the trivalent nickel tetra-aza macrocyclic complex. The e.s.r. spectrum of this solution, frozen at 77 K, indicates unambiguously the oxidation state and the stereochemical features of the species present in solution (Figure 4).

The spectrum displays axial symmetry with a $g_\perp$ value considerably greater than $g_\|$, as expected for the formation of a low-spin d^7 cation in an elongated octahedral environment. Moreover, $g_\|$ is split into seven lines, which indicates the presence of two equivalent chlorine atoms along the z axis ($I_{Cl} = \frac{3}{2}$). Thus, oxidation of the $[Ni^{II}(L^1)Cl_2]$ complex by Cl_2 in CH_2Cl_2 produces an authentic trivalent complex of formula $[Ni^{III}(L^1)Cl_2]^+$. The Ni^{II}–Ni^{III} oxidation process can be followed *via* cyclic voltammetry in CH_2Cl_2 solution (0.1 mol dm^{-3} in $NBu^n{}_4Cl$) at 25 °C, using a platinum microsphere as a working electrode. A quasi-reversible profile is observed ($i_a/i_c = 1$; $\Delta E_p = 80$ mV). The only moderately positive $E_{\frac{1}{2}}$ value, compared to the ferrocene–ferrocenium internal reference standard (0.175 V), indicates a noticeable stability of the $[Ni^{III}(L^1)Cl_2]Cl$ complex. This type of electrochemical investigation has been extended to other $Ni(L^1)X_2$ complexes in CH_2Cl_2 solution, 0.1 mol dm^{-3} in $NBu^n{}_4X$ ($X = HSO_4$, NO_3, ClO_4, or BF_4). Cyclic voltammetry showed quasi-reversible profiles and corresponding $E_{\frac{1}{2}}$ values, measured at 25 °C, *vs.* the internal ferrocene standard, are shown in Figure 5. The one-electron oxidation of $Ni^{II}(L^1)X_2$ was not observed for X = Br, I, or SCN, due to the anticipated anodic discharge ascribed to the bulk oxidation of the anion of the supporting electrolyte ($2X^- \rightleftharpoons X_2 + 2e^-$). Measured $E_{\frac{1}{2}}$ values refer to the half-reaction (4). A direct comparison between the systems is not totally valid,

$$[Ni^{III}(L^1)X_2]X + e^- \rightleftharpoons [Ni^{II}(L^1)X_2] + X^- \qquad (4)$$

since each experiment has not been carried out in the same ionic background, but with its own 0.1 mol dm^{-3} $NBu^n{}_4X$ supporting electrolyte. Thus, comparison is based on the assumption that the potential associated with the ferrocene–ferrocenium couple does not vary significantly on changing the anion. This approximation seems quite reasonable, if one considers that X^- ions can interact only through a weak ionic pairing with the ferrocenium ion.

The potential diagram shown in Figure 5 shows how spectacular the effect exerted by the axial X groups can be on the relative stabilization of the trivalent state. The difference of the electrode potential values associated with the most stable and least stable trivalent species (chloride and perchlorate complexes, respectively) is 750 mV! This difference is even larger than that observed in MeCN solution (0.1 mol dm^{-3} in $NBu^n{}_4ClO_4$), for nickel(II,III) complexes with a complete series of polyaza macrocycles.[13] In the latter case, oxidation selectivity was modulated through variations in the ligands denticity (ter-, quadri-, quinque-, and sexi-dentate amine macrocycles) and atomicity (from 9- to 18-membered rings). Thus, change of the anions X^- in the axial positions of the elongated octahedron of nickel tetra-aza macrocyclic complexes seems a very powerful tool to control access to the trivalent state.*

The trend of the anion-controlled stabilization of nickel(III) complexes (Figure 5) parallels the *spectrochemical series* of inorganic anions: $Cl^- > NO_3^- > HSO_4^- > ClO_4^-$. Hence the greater co-ordinating tendency of X^-, the greater is the relative solution stability of the $[Ni^{III}(L^1)X_2]X$ species. This behaviour reflects the ability of tripositive metal ions, such as Ni^{III}, to profit from the ligand-field stabilization energy (in the present case: the axial field) to a larger extent than a dipositive cation. Stabilization effects due to axial binding of strongly co-ordinating anions have been observed even with cyclam (L^2) complexes in water, but only in the presence of substantial amounts of X^-.[14]

The determination of the Ni^{III}–Ni^{II} redox potentials under the described conditions in this work opens the way to a reconsideration of the spectrochemical series for inorganic anions. However, this procedure cannot consider anions of pronounced reducing tendencies (SCN^-, Br^-, I^-, *etc.*) and has

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* The different stabilization effect exerted by varying X^- does not depend solely on differences in the intensity of the axial Ni–X interactions, but also on differences in the electrostatic interactions in the ionic couple $[Ni(L^1)X_2]^+X^-$, the intensity of which may vary with the nature of X^-. However, we believe that the latter effect is much less important than the former. In any case, this electrostatic effect should cancel any similar effect given by the corresponding $[Fe(\eta\text{-}C_5H_5)_2]^+X^-$ ionic couple.

to be limited to anions especially resistant towards oxidation (which are, in general, not too co-ordinating). In this connection, it is interesting to consider the behaviour of the tetrafluoroborate ion. In the cyclic voltammetry investigation of a CH_2Cl_2 solution 10^{-3} mol dm^{-3} in $Ni^{II}(L^1)(BF_4)_2$ and 0.1 mol dm^{-3} in $NBu^n{}_4BF_4$, an irreversible wave is observed in the oxidation scan at about 1.13 V *vs.* ferrocene–ferrocenium which is immediately followed by anodic discharge. The $[Ni^{II}(L^1)][BF_4]_2$–$[Ni^{III}(L^1)(BF_4)_2]BF_4$ oxidation process thus occurs at a potential 0.2 V more positive than that for the perchlorate system. This indicates that the stabilizing effect exerted by ClO_4^- on Ni^{III} through axial co-ordination is 0.2 V (= 1 600 cm^{-1}) greater than that for BF_4^- and would suggest that *perchlorate is a more strongly co-ordinating ligand than tetrafluoroborate.*

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