Stabilisation of Trivalent Nickel through 1 : 2 Co-ordination by Cyclic Terdentate Ligands $\overline{\mathrm{CH_2CH_2NH(CH_2)_2NH(CH_2)_2X}}$ (X = NH, O, or S)†

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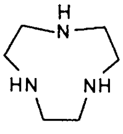
The octahedral six-co-ordinated complexes $[Ni(L^2)_2]^{2+}$ and $[Ni(L^3)_2]^{2+}$ (L^2 and L^3 = 1-oxa- and 1-thia-4,7-diazacyclononane, respectively) (donor set: N_4O_2 and N_4S_2, respectively) undergo a reversible one-electron oxidation process in MeCN and dimethyl sulphoxide (dmso) solution to give authentic Ni^{III} species. These Ni^{III} complexes present a distorted stereochemical arrangement, with the O and S heteroatoms occupying the axial sites of an elongated octahedron, and persist in solution for hours. Comparison with the corresponding complexes of 1,4,7-triazacyclonanane (L^1) (donor set: N_6) indicates that the relative stability of the trivalent species, expressed by the value of $E_{\frac{1}{2}}(Ni^{III}–Ni^{II})$, decreases along the series: $L^1 > L^3 > L^2$, the trend reflecting the decrease in the strength of the Ni–X interactions (X = N, S, or O). The corresponding Ni^{III} complexes of the open-chain analogues of the macrocycles L^1 or L^3 form at comparable potentials, but persist in solution only in the time-scale of the voltammetry experiment, thus demonstrating the existence of a purely kinetic macrocyclic effect in the stabilisation of high oxidation states of metals.

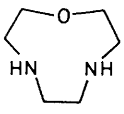
It has recently been shown that co-ordination by six secondary amine nitrogen atoms of two molecules of 1,4,7-triazacyclononane, L^1, is particularly favourable for the formation of solution-stable Ni^{III} complexes.[1,2] Solution stability is a rather vague term, which encompasses both: (*i*) the tendency of the Ni^{II}–Ni^{III} oxidation process to occur and which is exactly expressed by the reduction potential of the Ni^{III}–Ni^{II} redox couple in the chosen solvent (thermodynamic contribution), and (*ii*) the tendency of the Ni^{III} species generated to persist in solution (kinetic contribution). On the thermodynamic side, the very high solution stability of $[Ni^{III}(L^1)_2]^{3+}$ seems to result from the preference of the Ni^{III} ion, d^7 low-spin, for six-co-ordination. The size of the macrocyclic ring is crucial, since the corresponding triazacyclo-decane and -undecane complexes, $[Ni^{III}(tacd)_2]^{3+}$ and $[Ni^{III}(tacu)_2]^{3+}$ complexes are formed at considerably, and progressively, more positive potentials.[3] Recent *X*-ray studies have shown that the $[Ni^{III}(L^1)_2]^{3+}$ complex ion presents an axially elongated octahedral stereochemistry, such a distortion being expected for a low-spin, d^7 cation, due to the Jahn–Teller effect.[4] Furthermore, comparative investigations on the $E_{\frac{1}{2}}(Ni^{III}–Ni^{II})$ values of complexes with cyclic polyamine systems of varying denticity[3] have shown that the co-ordinative arrangement offered by two L^1 molecules is the most favourable for attainment of the Ni^{III} state. In particular it is more favourable than that offered by the single hexamine ring of 1,4,7,10,13,16-hexa-azacyclo-octadecane.[5]

Moreover, beside the ligand's structure and denticity, the nature of the donor atoms should play a very important role in the relative stabilisation of trivalent nickel. In this connection, the oxidation of the Ni^{II} complex with the sulphur analogue of L^1 (*i.e.* tscn) has been investigated.[6] A $[Ni(tscn)_2]^{3+}$ species is formed at a potential 0.4 V more positive than the $[Ni^{III}(L^1)_2]^{3+}$ species, through a quasi-reversible one-electron change. However, in the absence of e.s.r. characterisation, there is no way of unambiguously assessing whether the oxidation process involved the metal centre (to give an authentic Ni^{III} species) or the ligand framework (to give a Ni^{II}-oxidised ligand complex).

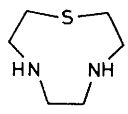
In this work, we wished to consider the effect of replacing one secondary amine nitrogen atom of the favoured framework of triazacyclononane, L^1, by either an ethereal oxygen atom, 1-oxa-4,7-diazacyclononane, L^2, or a thioethereal sulphur atom, 1-thia-4,7-diazacyclononane, L^3. In particular, the aim of the present work is to evaluate possible stabilisation effects on the Ni^{III} state due to the co-ordination of Group 16 heteroatoms, X (X = O or S), in an octahedral ligating environment N_4X_2.



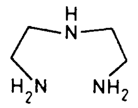
L^1



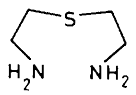
L^2



L^3



L^4



L^5

Sulphur *vs.* oxygen co-ordination effects on the formation of trivalent nickel have recently been investigated with some triazene oxide ligand complexes (donor set: N_2O_4 and $N_2O_2S_2$).[7] However, a true comparison could not be made since, although the Ni^{III} complex with the sulphur-containing ligand is stable enough to be characterised, the oxidised complex of the oxygen analogue does not persist in solution even in the time-scale of the cyclic voltammetry experiment.

Finally, we have investigated the Ni^{II}–Ni^{III} oxidation process with the six-co-ordinated complexes of the open-chain terdentate analogues of L^1 and L^3 (L^4 and L^5 respectively) in order to assess definitively the role of the cyclic or non-cyclic nature of the ligand on the stabilisation of unusually high oxidation states of metals (the kinetic side of the solution stability).

Experimental

Ligands and Complexes.—Ligands L^2 [8] and L^3 [9] were obtained according to previously described synthetic pro-

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† *Non-S.I. unit employed*: G = 10^{-4} T.

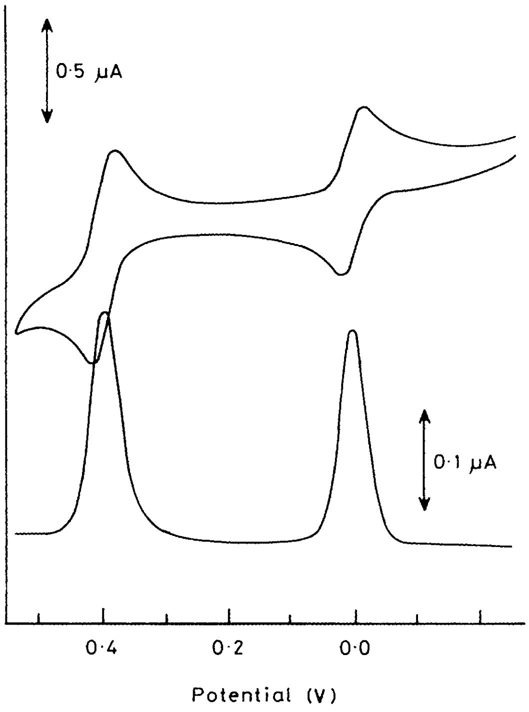

Figure 1. Cyclic voltammetry (upper curve, 50 mV s^{-1}) and alternating current voltammetry (lower curve, 2 mV s^{-1}) oxidation profiles for a 10^{-3} mol dm^{-3} solution of $[Ni^{II}(L^3)_2][ClO_4]_2$ in acetonitrile (0.1 mol dm^{-3} $[NEt_4]BF_4$, 25 °C). The less anodic wave corresponds to the oxidation of ferrocene, added in equimolar amount, as an internal standard

Table. Half-wave potentials, $E_{\frac{1}{2}}$/V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$[a] associated with the half-reaction $[Ni^{III}L_2]^{3+} + e^- \rightleftharpoons [Ni^{II}L_2]^{2+}$ in acetonitrile and dimethyl sulphoxide solutions, 0.1 mol dm^{-3} in $[NEt_4]BF_4$, at 25 °C

	$E_{\frac{1}{2}}$	
Ligand, L	In MeCN	In dmso
L^1	0.558	0.220
L^2	1.084	*b*
L^3	0.785	0.500
L^4	0.610	0.240
L^5	0.820	0.510

[a] ±3 mV. [b] Wave obscured by the anodic discharge.

cedures, in the form of dihydrobromides. In the synthesis of the Ni^{II} complexes, a stoicheiometric amount of the diamine dihydrobromide was dissolved in the minimum amount of 6 mol dm^{-3} NaOH. The alkaline solution was then extracted with five portions of chloroform. After standing overnight on anhydrous sodium sulphate, the chloroform was evaporated to give the pure ligand, which was dissolved in ethanol. To the boiling ethanolic solution, a stoichiometric amount of a standard aqueous solution of $Ni(ClO_4)_2$ was added dropwise. After reflux for 30 min, the solution was allowed to cool and violet crystals of the $[Ni(L)_2][ClO_4]_2$ ($L = L^2$ or L^3) complex salt formed. **CAUTION!** Metal perchlorate complexes are explosive and care should be employed when handling them. In particular, such compounds should never be heated as solids.

Electrochemical and Spectroscopic Characterisation of the Nickel(III) *Complexes*.—The Ni^{II}–Ni^{III} redox change was investigated in MeCN and dmso (dimethyl sulphoxide) solution, 0.1 mol dm^{-3} in $[NEt_4]BF_4$, through voltammetric techniques [cyclic voltammetry (c.v.) and alternating current voltammetry (a.c.)] using a three-electrode cell configuration. The working electrode was a platinum microsphere, the auxiliary electrode a platinum foil, and the reference electrode was a silver wire, which was calibrated *vs.* the $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ internal standard redox couple through addition of an equimolar amount of ferrocene to the solution of the metal complex under investigation.

In the controlled-potential electrolysis experiment, the working cell, containing a platinum gauze anode and the reference silver wire, was connected to the counter-electrode compartment through a bridge filled with the electrolyte solution. When the electrolysis was complete, as indicated by the appearance of a 'plateau' in the integrated current *vs.* time plot, portions of the oxidised green solution were withdrawn by a syringe under anaerobic conditions and transferred to a 1-mm quartz cell, to measure the u.v.–visible absorption spectrum, or to a quartz tube for the e.s.r. investigation.

For electrochemical experiments, an AMEL (Milan) apparatus was used composed of a model 552 potentiostat, a model 563 function generator, and a model 566 interface. The current–potential curves were recorded on a Hewlett-Packard 7040 *XY* recorder. Dmso and MeCN were refluxed over CaH_2, distilled and kept over 3A molecular sieves under a nitrogen atmosphere. $[NEt_4]BF_4$ (Carlo Erba, Milan, polarographic grade) was used as supplied. The temperature of the cell, in the c.v.–a.c. experiments, was kept at 25 °C through circulation of thermostatted water.

Absorption spectra of the Ni^{III} complex solutions were measured on a Cary 2300 (Varian) spectrophotometer.

E.s.r. spectra of frozen (liquid nitrogen temperature) solutions were recorded on a Varian E 109 *X*-band spectrometer. Values of *g* were determined relative to diphenylpicrylhydrazyl (dpph).

Results and Discussion

Formation of $[Ni^{III}(L)_2]^{3+}$ *Complexes. Effect of the Nature of the Heteroatom* X (X = O *or* S).—The complexes $[Ni^{II}(L^2)_2][ClO_4]_2$ and $[Ni^{II}(L^3)_2][ClO_4]_2$, dissolved in a MeCN solution, 0.1 mol dm^{-3} in $[NEt_4]BF_4$, undergo a reversible one-electron oxidation process at the platinum working electrode. Figure 1 shows the reversible profiles obtained using cyclic voltammetry and alternating current voltammetry techniques for the L^3 complex. Similar reversible profiles have been obtained for the $[Ni^{II}(L^2)_2]^{2+}$ complex, whose one-electron oxidation occurs at a potential 0.4 V more positive. Pertinent $E_{\frac{1}{2}}$ values are compared, in the Table, to that measured for the one-electron oxidation of the $[Ni^{II}(L^1)_2]^{2+}$ complex under the same conditions.

Bulk oxidation by a platinum gauze, under controlled-potential conditions, makes the blue solutions of the investigated Ni^{II} complexes turn green. Persistence of the oxidised green species was monitored through their absorption spectra in the u.v.–visible region. Figure 2 shows the spectra of the L^2 complex, taken at chosen time intervals. The two-transition profile, typically observed with trivalent nickel–polyamine complexes,[10,11] decays according to a first-order pattern, with a $t_{\frac{1}{2}}$ value of 170 min. Similar behaviour is displayed by the L^3 complex, which has a lower kinetic stability ($t_{\frac{1}{2}}$ = 80 min).

The authenticity of the trivalent state for the electrogenerated complexes has been definitively demonstrated through e.s.r.

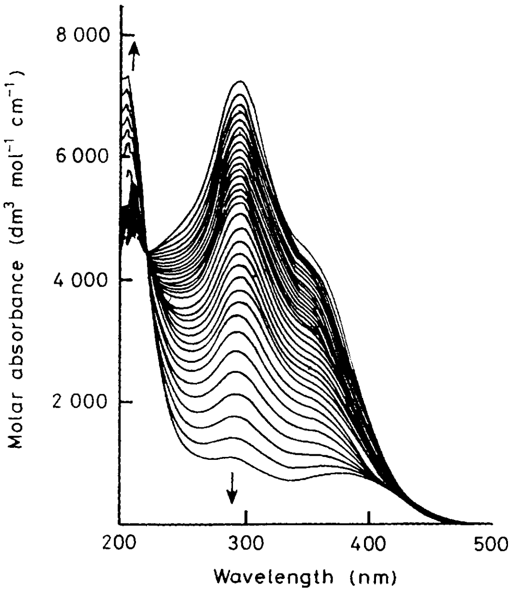

Figure 2. Absorption spectra of an acetonitrile solution of the [Ni^{III}(L^2)$_2$]$^{3+}$ complex, generated through controlled-potential electrolysis. The first seventeen spectra were taken every 5 min, the following nine every 10 min, the last seven every 15 min

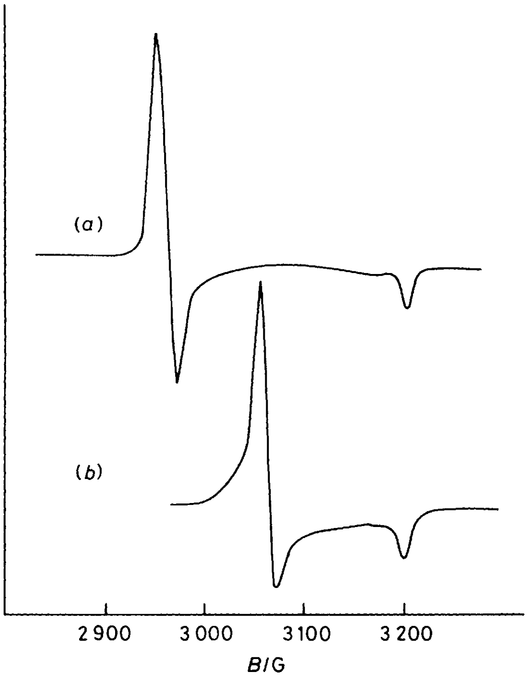

Figure 3. E.s.r. spectra of frozen (77 K) acetonitrile solutions of the [Ni^{III}(L^2)$_2$]$^{3+}$ [spectrum (*a*)] and [Ni^{III}(L^3)$_2$]$^{3+}$ [spectrum (*b*)] complexes, generated through controlled-potential electrolysis. (*a*) $g_\perp = 2.18$, $g_\parallel = 2.02$; (*b*) $g_\perp = 2.11$, $g_\parallel = 2.02$

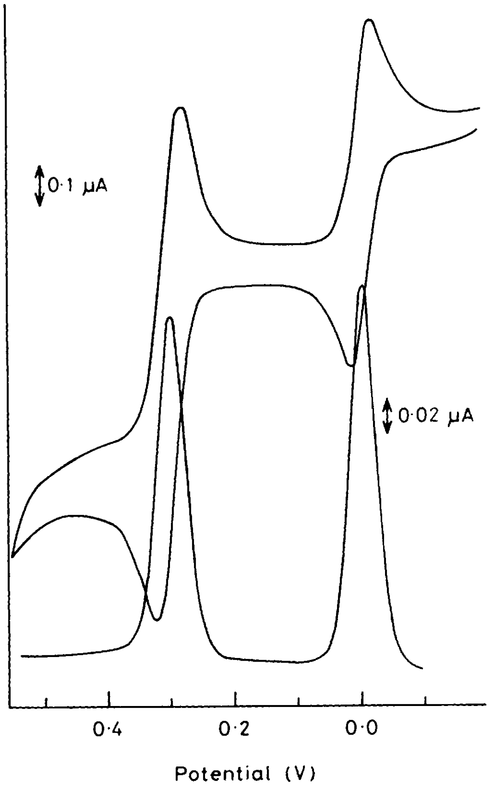

Figure 4. Cyclic voltammetry (upper curve, 50 mV s^{-1}) and alternating current voltammetry (lower curve, 2 mV s^{-1}) oxidation profiles for a 10^{-3} mol dm^{-3} solution of [Ni^{II}(L^4)$_2$][ClO$_4$]$_2$ in acetonitrile (0.1 mol dm^{-3} [NEt$_4$]BF$_4$, 25 °C). The less anodic wave corresponds to the oxidation of ferrocene, added in equimolar amount, as an internal standard

experiments. Figure 3 reports the e.s.r. spectra of the MeCN solutions of the [Ni^{III}(L^2)$_2$]$^{3+}$ and [Ni^{III}(L^3)$_2$]$^{3+}$ complexes, frozen at 77 K. In both cases, $g_\perp$ is considerably greater than $g_\parallel$, as expected for a low-spin, d^7 metal centre in an elongated octahedral environment. The distinctly lower value of $g_\perp$ for the L^3 complex, compared to the L^2 analogue (2.11 *vs.* 2.18) should be ascribed to the more pronounced covalent character of the metal–ligand interaction.[12] Moreover, absence of any splitting in the $g_\parallel$ feature would exclude the presence of amine nitrogen atoms in the two axial sites of the elongated octahedron. Thus axial positions of the [Ni^{III}(L^2)$_2$]$^{3+}$ and [Ni^{III}(L^3)$_2$]$^{3+}$ complexes should be occupied by the oxygen and sulphur atoms, respectively.

In conclusion, the redox change investigated for 1:2 complexes of macrocycles L^2 and L^3 can be described, in its stereochemical* and electronic aspects, by equation (1).

$$\begin{array}{ccc} [\mathrm{Ni^{II}(L)_2}]^{2+} & \rightleftharpoons & [\mathrm{Ni^{III}(L)_2}]^{3+} + e^- \\ \text{octahedral} & & \text{octahedral} \\ d^8 & & d^7\text{, low-spin} \end{array} \qquad (1)$$

$E_{\frac{1}{2}}$(Ni^{III}–Ni^{II}) values, reported in the Table, indicate that the relative stability of the trivalent complex decreases along the series: L^1 > L^3 > L^2. In other words, replacing two amine groups of an N$_6$ octahedral environment by two sulphur or two oxygen atoms makes attainment of the Ni^{III} state progressively more difficult. This can be related to a more, or less, favourable variation of the Ni–X interactions, which occurs during the Ni^{II}–Ni^{III} oxidation process. As far as the Ni^{II} oxidation state is concerned, detailed analysis of the *d–d* spectra of the bis(cyclononane) complexes, using the crystal field model, gave the following sequence for the global 10 *Dq* values; N$_6$: 12 500; N$_4$S$_2$: 11 770; N$_4$O$_2$: 11 600 cm^{-1}.[13] Assuming that the N$_4$

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* The stereochemistries of the divalent complexes have been ascertained through *X*-ray measurements: [Ni^{II}(L^1)$_2$]$^{2+}$, L. J. Zompa and T. N. Margulis, *Inorg. Chim. Acta*, 1978, **28**, L157; [Ni^{II}(L^2)$_2$]$^{2+}$, ref. 8; [Ni^{II}(L^3)$_2$]$^{2+}$, ref. 13.

equatorial field is the same for all the complexes, the above trend should reflect that of the energy of the Ni^{II}–X interactions. On the other hand, crystal field theory predicts that a d^8 (octahedral) to a d^7 low-spin (octahedral) change profits from a favourable crystal field stabilisation energy (c.f.s.e) contribution of 6 *Dq*. A further favourable contribution (by a factor ranging from 1.4 to 1.6)[14] derives from the 2+ to 3+ increase of the electrical charge of the metal centre. Thus, the sequence of $E_{\frac{1}{2}}(Ni^{III}–Ni^{II})$ values determined ($L^1 < L^3 < L^2$) reflects the trend of the donor tendencies of the co-ordinative systems: $N_6 > N_4S_2 > N_4O_2$. The stronger the metal–ligand interaction, the easier is the oxidation of the metal centre. An analogous behaviour has been documented in the formation of Ni^{III} and Cu^{III} complexes with all-nitrogen macrocycles of varying denticity and ring size.[15]

Formation of Ni^{III} *Complexes of Open-chain Analogues of Cyclononane Ligands. The Existence of a Kinetic Macrocyclic Effect on the Stabilisation of Trivalent Nickel.*—Most work on the solution chemistry of transition metals in unusually high oxidation states, in particular Ni^{III}, has been done with complexes with cyclic, multidentate ligands. However, since access to the higher oxidation state is simply related, from a thermodynamic point of view, to the strength of the metal–ligand interactions, there are no special reasons that prevent the formation of stable Ni^{III} complexes with the open-chain analogues of the cyclononane molecules investigated here. Thus, we have investigated the oxidation behaviour of the 1:2 complexes of Ni^{II} with diethylenetriamine (L^4, the open-chain analogue of L^1) and 1,5-diamino-3-thiapentane (L^5, the analogue of L^3). Both $[Ni^{II}(L^4)_2][ClO_4]_2$ and $[Ni^{II}(L^5)_2][ClO_4]_2$ complexes in MeCN and dmso solution undergo a reversible one-electron oxidation process at the platinum electrode (see Figure 4 as an example of the voltammetric response), which is assigned to the Ni^{II}–Ni^{III} redox change. Values of $E_{\frac{1}{2}}(Ni^{III}–Ni^{II})$, measured *vs.* the internal $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ reference couple, are compared, in the Table, with those measured for L^1 and L^3 in the same media. It can be seen that, for a given donor set, the open-chain ligand–Ni^{III} complex is formed at a potential which is only 10—50 mV more positive than that observed for the macrocyclic complex. The small difference of $E_{\frac{1}{2}}(Ni^{III}–Ni^{II})$ values probably reflects the fact that the cyclononane ligand exerts a slightly stronger field than its non-cyclic analogue, due to the presence of two secondary, rather than primary, nitrogen atoms.[13]

However, if controlled-potential electrolysis experiments are performed on solutions of $[Ni^{II}(L^4)_2][ClO_4]_2$ or $[Ni^{II}(L^5)_2][ClO_4]_2$ in MeCN or dmso, the integrated current signal does not reach a 'plateau', but constantly increases, due to rapid decomposition of the electrogenerated Ni^{III} complex. This indicates that the Ni^{III} species, which is stable in the time-scale of the voltammetric measurements, is not stable in the time-scale of the controlled-potential electrolysis. Moreover, chemical oxidation, by $NO(BF_4)$, of the violet MeCN solutions of the Ni^{II} complexes of L^4 and L^5 does not induce formation of the green colour of the Ni^{III} chromophore, as observed for instance with bis(cyclononane) complexes, but simply causes the solution to decolourise, probably through metal complex decomposition *via* the unstable Ni^{III} species.

The above evidence indicates that stabilisation of unusually high oxidation states of metals through macrocyclic co-ordination is essentially kinetic in origin, and merely reflects the reduced reactivity of the transition-metal ion towards reducing substrates (solvent, uneliminated impurities, the ligand itself), when trapped in the macrocyclic co-ordinative framework. The extreme inertness of polyazamacrocyclic complexes, for instance towards demetallation, is well documented in the case of divalent cations. In particular, the $[Ni^{III}(L^1)_2]^{3+}$ complex persists in fairly acidic solution and decomposes very slowly, due to protonation of the ligand, in 1 mol dm^{-3} HCl[16] {whereas the $[Ni^{III}(L^4)_2]^{3+}$ complex demetallates instantaneously}.

Finally, the Table indicates that six-co-ordinate, trivalent nickel complexes with both cyclic and non-cyclic terdentate ligands are formed in dmso solution at substantially less positive potentials than in MeCN solution. This behaviour, which has already been observed and discussed for corresponding complexes of N_6 co-ordinating systems,[3] reflects the capability of dmso to establish stronger solute–solvent interactions than MeCN, with the consequent enhanced stabilisation of the tripositive metal centre.

Conclusions

This work has demonstrated that the six-co-ordinate environment offered by two molecules of a cyclononane ligand is very favourable to the formation of trivalent nickel, through one-electron oxidation of the divalent complex. Moreover, the Ni^{III} cation presents a greater affinity towards the amine nitrogen atom than towards the 'softer' thioethereal sulphur and 'harder' ethereal oxygen atom.

Whereas the attainment of the trivalent state is solely controlled by the strength of the metal–ligand interactions, a cyclic arrangement of the ligand framework is required to impart kinetic stability and to allow the oxidised complex to persist in solution.

Acknowledgements

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