

Ring Size Effects on the Chemical Properties of Tervalent Nickel Complexes with Tetra-aza Macrocyclic Ligands in Aqueous Solutions. An Electrochemical and Pulse Radiolytic Study

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Electrochemical oxidation and oxidation by hydroxyl radicals of the divalent nickel complexes of 1,4,7,10-tetra-azacyclotetradecane and 1,4,8,12-tetra-azacyclopentadecane in acidic aqueous solutions containing perchlorate or sulphate anions are reported. The properties of the tervalent complexes thus formed are described. The results are compared with those reported earlier for other tervalent nickel complexes with tetra-aza macrocyclic ligands. The results indicate that neither the redox potentials nor the half-lives of the tervalent complexes are directly related to the cavity size of the ligand or its ligand-field strength. It is suggested that the detailed conformation of the macrocyclic ligands has a profound effect on the properties of the tervalent complexes. The difference in the factors affecting the chemical properties of the mono- and ter-valent complexes is discussed.

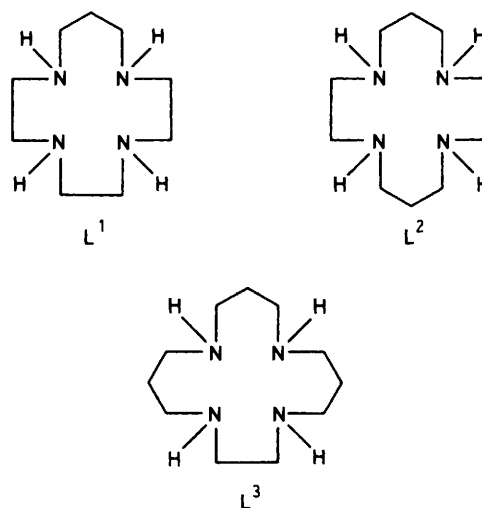
The chemical properties of complexes of tervalent nickel with a variety of ligands in aqueous solutions have been recently reported.¹⁻⁹ Some of these complexes have been shown to be relatively stable, powerful single-electron oxidizing agents. We have carried out a detailed study of the properties of tervalent nickel complexes with 14-membered tetra-aza macrocyclic ligands.⁴⁻⁹ The results indicated that inorganic anions, especially sulphate and phosphate, act as strong axial ligands for these complexes.⁹ These anions also have a significant kinetic stabilizing effect as measured from the lifetimes of the tervalent nickel complexes. It was also found that the lifetimes in aqueous solutions are not directly correlated to the redox potential of the complexes.^{6,8,9} Tervalent nickel complexes with macrocyclic ligands have recently been adopted as oxidizing agents in different chemical systems.¹⁰

It thus seemed of interest to study the effect of changing the cavity size of the macrocyclic ligand on the chemical properties of tervalent nickel complexes in aqueous solutions. In the present study we report the properties of tervalent nickel complexes of 1,4,7,10-tetra-azacyclotridecane, L¹, and 1,4,8,12-tetra-azacyclopentadecane, L³, and compare them with those of the complex with 1,4,8,11-tetra-azacyclotetradecane, L², which has been reported earlier.^{4,6,7} Electrochemistry and pulse radiolysis were chosen as the techniques for obtaining both thermodynamic and kinetic data.

Experimental

Materials.—The ligand L¹ was prepared and purified according to the procedure described in the literature;¹¹ L³ was supplied by Strem. The complexes [NiL¹][ClO₄]₂¹² and [NiL³][ClO₄]₂¹² were prepared from the free ligands and [Ni(H₂O)₆][ClO₄]₂. Their purity was checked by n.m.r. and u.v.-visible spectroscopy which were in full agreement with literature values.¹³

All other materials were of A.R. grade and were used without further treatment. All solutions were prepared using heat-



distilled water which was then passed through a Millipore set up, the final resistance being > 10 MΩ.

Electrochemical Measurements.—A three-electrode Metrohm cell was used. The working electrode was either a Pt bead or a 34-cm² platinum screen (for preparative work). A coiled platinum-wire counter electrode was separated by an agar (2 mol dm⁻³ KCl) bridge and the Ag-AgCl (3 mol dm⁻³ KCl) reference electrode was connected by a Luggin capillary also containing agar (2 mol dm⁻³ KCl). Unless otherwise stated, all potential measurements are given *versus* the Ag-AgCl reference. The electrochemical equipment consisted of a P.A.R. model 373 potentiostat, an IEC F 553 function generator for linear potential-sweep cyclic voltammetry with output to a Bryans 2600 A-4 X-Y recorder, and a Fluke 8000A digital multimeter.

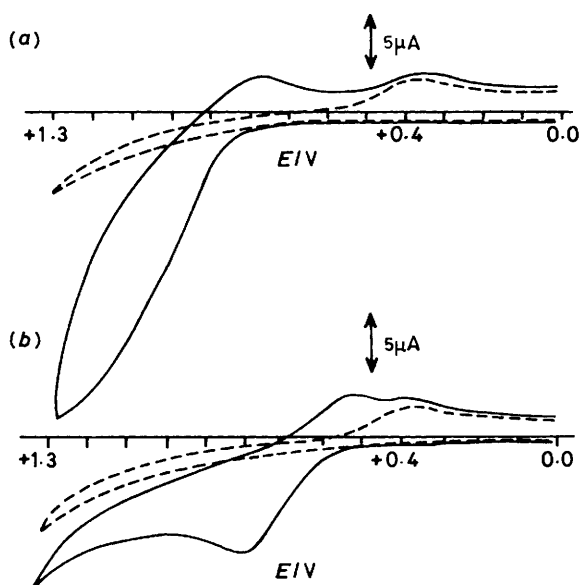


Figure 1. Cyclic voltammograms of $1 \times 10^{-3} \text{ mol dm}^{-3} [\text{NiL}^1][\text{ClO}_4]_2$ at pH 2.0 with (a) $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ and (b) $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$; scan rate 102 mV s^{-1} . Dashed curves show supporting electrolyte only

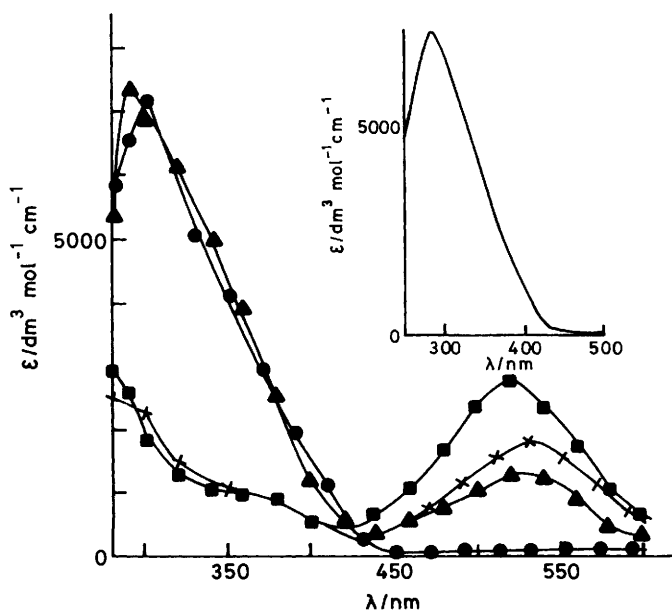


Figure 2. Spectra of $[\text{NiL}^1]^{3+}$ as obtained in pulse radiolysis experiments. N_2O -saturated solutions containing $2 \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^1][\text{ClO}_4]_2$ at pH 3.3: \blacksquare , 20 μs after the pulse; \blacktriangle , 40 ms after the pulse; \times , 20 μs after the pulse and containing $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$; \bullet , 1 ms after the pulse and containing $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. Insert: spectrum of $[\text{NiL}^1]^{3+}$ at pH 2.0 as obtained by electrochemical and chemical oxidations

Pulse Radiolysis.— 0.1 – $1.5 \mu\text{s}$, 200 mA pulses of 5 MeV electrons from the linear accelerator at the Hebrew University of Jerusalem were used. The dose per pulse was 100 – 3000 rad . Methods for preparing the solutions and analysis of the results were identical to those described earlier in detail.^{5,6,9}

Spectroscopic Measurements.—U.v.–visible spectra were recorded using a Bausch and Lomb Spectronic 2000 spectrophotometer. E.s.r. spectra were recorded using a Varian model E12 X-band spectrometer.

Results and Discussion

Electrochemical Oxidations.—(a) *Oxidation of $[\text{NiL}^1]^{2+}$.* Typical cyclic voltammograms of solutions containing $[\text{NiL}^1]^{2+}$ with NaClO_4 and Na_2SO_4 as supporting electrolytes at pH 2.0 are shown in Figure 1. The complex is clearly oxidized in a quasi-reversible process in both solutions. Thus the separation between the oxidation and reduction waves is much larger than 60 mV and it is therefore difficult to evaluate the exact redox potential of $[\text{NiL}^1]^{2+}$ under these conditions. However, the results clearly indicate that sulphate lowers the redox potential; a rough estimate* of the redox potentials is 0.90 and 0.65 V vs. Ag–AgCl in $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ and $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ respectively. From these results the stability constant for binding SO_4^{2-} to $[\text{NiL}^1]^{3+}$ can be estimated, as shown below, where $n = 1$ or 2. Due to the irreversible nature of

$$K = \frac{[\text{NiL}^1(\text{SO}_4)_n]}{[\text{NiL}^1]^{3+}[\text{SO}_4^{2-}]^n} \approx 5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ (or } \text{dm}^6 \text{ mol}^{-2}\text{)}$$

the redox process an effort to evaluate n by changing the sulphate concentration failed. It is of interest to note that the oxidation of $[\text{NiL}^1]^{2+}$ in acetonitrile was also reported to be quite irreversible.¹⁴

A preparative electrochemical oxidation of $5 \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^1][\text{ClO}_4]_2$ in $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ (pH 2.0) yields a green solution whose u.v.–visible spectrum is plotted in Figure 2. The half-life of $[\text{NiL}^1]^{3+}$, thus obtained, is 6 min. A preparative electrochemical oxidation of $3 \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^1][\text{ClO}_4]_2$ in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ (pH 2.0) yields a green solution with a u.v.–visible spectrum which is nearly identical to that of the product from the perchlorate solution. However, this product is considerably more stable, i.e. $t_{1/2} \sim 14 \text{ d}$. The same product is also obtained by oxidizing $[\text{NiL}^1]^{2+}$ with $\text{Na}_2\text{S}_2\text{O}_8$ in a solution containing $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at pH 2.0.

The e.s.r. spectrum of a solution containing $2 \times 10^{-3} \text{ mol dm}^{-3} [\text{NiL}^1][\text{ClO}_4]_2$, $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, and $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_8$ was measured. At room temperature a band with $g = 2.163$ and a band width of 17.5 G was observed. At 77 K $g_{\text{av}} = 2.159$, $g_{\perp} = 2.228$, and $g_{\parallel} = 2.020$.

(b) *Oxidation of $[\text{NiL}^3]^{2+}$.* Typical cyclic voltammograms of solutions containing $[\text{NiL}^3]^{2+}$ with NaClO_4 and Na_2SO_4 as supporting electrolytes at pH 1.5 and 6.5 are shown in Figure 3. In the acidic solutions the oxidation of $[\text{NiL}^3]^{2+}$ is considerably more reversible than that of $[\text{NiL}^1]^{2+}$. In the sulphate containing solution the electrochemical process is reversible for scan rates slower than 10 mV s^{-1} . At pH 6.5 the perchlorate containing solution clearly indicates that an irreversible multi-electron process occurs, most probably a ligand oxidation process.^{6,9} In the sulphate containing solution the electrochemical process seems to be nearly reversible even at this pH, though the lifetime of the trivalent nickel complexes is considerably shorter in neutral solutions.^{6,8,9} Indeed, the reduction wave in this case is lower than the oxidation wave.

The dependence of the redox potential, E_r , on sulphate concentration, at pH 1.5 and constant ionic strength, $I = 0.3 \text{ mol dm}^{-3}$ kept by NaClO_4 , was measured. A linear dependence of E_r on $[\text{SO}_4^{2-}]$ was observed. It is expected that $E_r = E_r^0 - 0.059 \lg K - 0.059 n \lg [\text{SO}_4^{2-}]$, where E_r^0 is the redox potential in the absence of sulphate and $K = [\text{Ni}^{\text{III}}\text{L}^3(\text{SO}_4)_n]^{3-2n} / [\text{NiL}^3(\text{H}_2\text{O})_n]^{3+}[\text{SO}_4^{2-}]^n$. From the slope of the linear plot we obtain $n = 1$ and from the intercept and $E_r^0 = 1.0 \text{ V}$ we obtain $K = (6.7 \pm 1.7) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$. The value of the stability constant K is in agreement with those expected from

* The average of the potential of the oxidation and reduction waves.

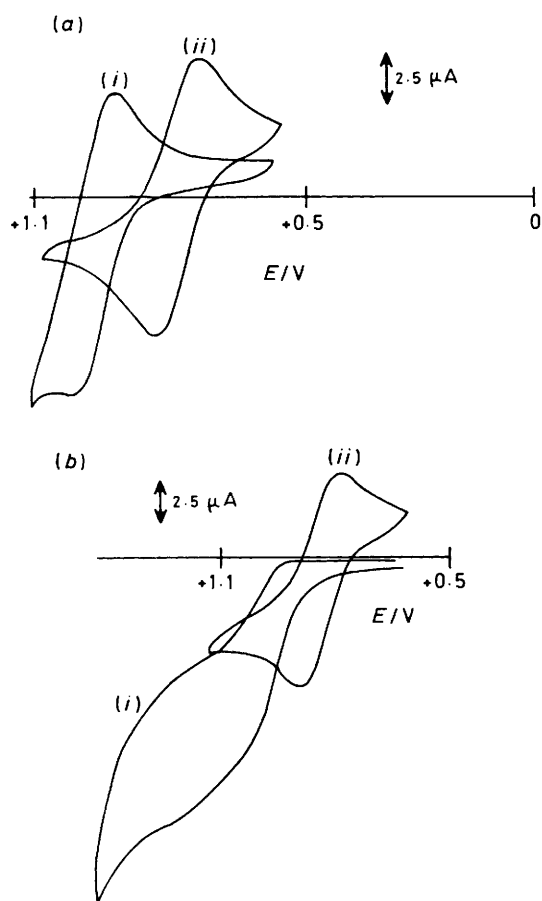


Figure 3. Cyclic voltammograms of $8 \times 10^{-3} \text{ mol dm}^{-3} [\text{NiL}^3][\text{ClO}_4]_2$. (a) pH 1.5: (i) $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$, scan rate 108 mV s^{-1} , (ii) $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, scan rate 108 mV s^{-1} . (b) pH 6.5: (i) $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$, scan rate 17.3 mV s^{-1} , (ii) $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, scan rate 106 mV s^{-1}

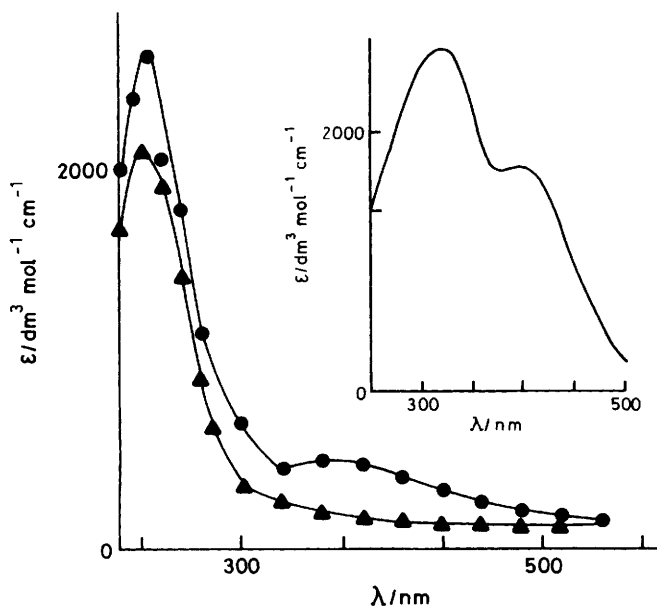


Figure 4. Spectra of $[\text{NiL}^3]^{3+}$ as obtained in pulse radiolysis experiments. N_2O -saturated solutions containing $1 \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^3][\text{ClO}_4]_2$ at pH 3.3: ●, 20 μs after the pulse; ▲, 20 μs after the pulse and containing $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. Insert: spectrum of $[\text{NiL}^3]^{3+}$ at pH 2.0 as obtained by electrochemical and chemical oxidations

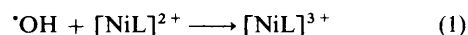
analogous results for tervalent nickel complexes with 14-membered tetra-aza macrocyclic ligands.⁴⁻⁹ On the other hand, for all the latter complexes $n = 2$ was found.⁷⁻⁹ The redox potential of $[\text{NiL}^3]^{2+}$ in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ was recently reported to be 0.77 V vs. saturated calomel electrode¹⁵ in excellent agreement with our results. However, in that report it was claimed that the replacement of Na_2SO_4 by NaClO_4 generally did not significantly alter E° .¹⁵ We have no explanation for this discrepancy.*

A preparative electrochemical oxidation of $2 \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^3][\text{ClO}_4]_2$ in $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ (pH 2.0) at 1.1 V yields a green solution the u.v.—visible spectrum of which is plotted in Figure 4. The half-life of $[\text{NiL}^3]^{3+}$ thus obtained is $4.0 \pm 0.5 \text{ min}$. A preparative electrochemical oxidation of $2 \times 10^{-4} [\text{NiL}^3][\text{ClO}_4]_2$ in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ (pH 2.0) at 1.0 V yields a green solution with a spectrum nearly identical to that formed in the perchlorate solution. The half-life of $[\text{NiL}^3(\text{SO}_4)]^+$ {or $[\text{NiL}^3(\text{SO}_4)_2]^-$ } thus formed is $10.0 \pm 1.0 \text{ min}$. The same product is also obtained by oxidizing $[\text{NiL}^3]^{2+}$ with $\text{Na}_2\text{S}_2\text{O}_8$ in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at pH 2.0.

The e.s.r. spectrum of a solution containing $7 \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^3]^{2+}$, $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_8$, and $0.3 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was measured. At room temperature a band with $g = 2.182$ was observed. At 77 K $g_{av} = 2.177$, $g_{\parallel} = 2.026$, and $g_{\perp} = 2.258$.

Pulse Radiolytic Oxidations.—(a) Oxidation of $[\text{NiL}^1]^{2+}$ by hydroxyl radicals. N_2O -saturated solutions containing $(1-10) \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^1][\text{ClO}_4]_2$ at pH 3.3 were irradiated. Under these conditions over 90% of the primary radicals formed by absorption of the radiation are transformed into hydroxyl radicals⁵ (the rest are hydrogen atoms which seem to be unreactive towards $[\text{NiL}^1]^{2+}$).

Three processes were observed optically under these conditions. The first process obeyed a pseudo-first-order rate law and is attributed to reaction (1), with $k = (3.5 \pm 0.4) \times$



$10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The spectrum of $[\text{NiL}^1]^{3+}$ thus formed is plotted in Figure 2. The second process, which obeys a first-order rate \dagger law with $k = (2.5 \pm 0.5) \times 10^2 \text{ s}^{-1}$, causes an increase in the absorption around 300 nm and a decrease around 550 nm , Figure 2. Similar processes were observed for other nickel complexes with tetra-aza macrocyclic ligands.^{5,6,9} These processes are attributed to a rearrangement (configurational isomerization) of the tervalent nickel complex, formed in the nearly diffusion-controlled reaction (1), to a more stable configuration.^{5,6,9} In the third process the tervalent nickel complex thus formed decomposes in a first-order process \ddagger with $k = 0.017 \pm 0.003 \text{ s}^{-1}$, probably *via* ligand oxidation.^{6,9}

The difference between the spectrum of the tervalent nickel complex formed electrochemically and by pulse radiolysis, Figure 2, is similar to that reported earlier for $[\text{NiL}^2]^{3+}$.^{6,9} At pH 3.3 part of the $[\text{NiL}^1]^{3+}$ is already present as $[\text{NiL}^1(\text{OH})]^{2+}$ and the hydroxo complexes of tervalent nickel complexes have an absorption band around 550 nm .⁹

When the experiments are repeated in solutions containing $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ the formation of transients with similar

* Professor E. Kimura has pointed out that their study concerned mainly the redox properties of complexes with imide anion macrocyclic ligands and therefore the sulphate effect was studied by them in detail only for those complexes.

\dagger The specific rates of these processes were independent of the solute concentration and pulse intensity.

Table. Properties of nickel complexes with saturated tetra-aza macrocyclic ligands (E° values measured vs. Ag–AgCl)

L^a	$E^\circ([\text{NiL}]^{3+}-[\text{NiL}]^{2+})/V$		$t_{1/2}([\text{NiL}]^{3+})$		$E^\circ([\text{NiL}]^{2+}-[\text{NiL}]^+)/V$	$\lambda_{\text{max}}[\text{NiL}]^{2+g}/\text{nm}$
	ClO_4^{-b}	SO_4^{2-c}	ClO_4^{-d}	SO_4^{2-e}		
L^1	~0.90	~0.65	6 min	14 d	< -1.70 ^h	426
L^2	0.70 ⁱ	0.45 ⁱ	10 h ⁱ	5 d ⁱ	-1.58 ^j	455
L^3	1.0	0.80	4 min	~10 min	-1.50 ^h	460
C-meso- L^4	~0.98 ^k	0.64 ^k	72 s ^k	>2 year ^k	-1.42 ^j	468
C- α -rac- L^4	$\geq 1.0^l$	0.75 ^l	-l,m	3 h ^l	—	—
C- β -rac- L^4	$\geq 1.0^l$	0.75 ^l	-l,m	2 h ^l	-1.44 ⁿ	461

^a $L^4 = 5,5,7,12,12,14$ -Hexamethyl-1,4,8,11-tetra-azacyclotetradecane. ^b pH 2.0, 0.5 mol dm⁻³ NaClO₄. ^c pH 2.0, 0.5 mol dm⁻³ Na₂SO₄. ^d Half-life for decomposition of $[\text{NiL}]^{3+}$ in 0.5 mol dm⁻³ NaClO₄, pH 2.0. ^e Half-life for decomposition of $[\text{NiL}]^{3+}$ in 0.5 mol dm⁻³ Na₂SO₄, pH 2.0. ^f pH 6.0, 0.3 mol dm⁻³ NaClO₄. ^g In CH₃NO₂. ^h Ref. 17. ⁱ Refs. 6 and 7. ^j Ref. 18. ^k Ref. 9. ^l Ref. 8. ^m Less than 1 min. ⁿ Ref. 19.

spectra is observed, Figure 2. However, the half-life of the product formed after 1 ms is several minutes instead of 42 s in the absence of SO₄²⁻. This result proves that this transient contains one or two sulphates as axial ligands. However, the specific rate of transformation from the first transient observed to the second one, $k = (1.0 \pm 0.2) \times 10^4 \text{ s}^{-1}$, is independent of sulphate concentration. This shows that a rate-determining rearrangement process occurs prior to sulphate ligation; similar observations were reported for other tetra-aza macrocyclic nickel(III) complexes.⁷ As the rearrangement reaction observed has a rate of $2.5 \times 10^2 \text{ s}^{-1}$ one has to conclude that either two consecutive rearrangement processes occur in the absence of sulphate or that the sulphate accelerates the rate of the rearrangement.

The observation that the ligation by sulphate requires a rate-determining rearrangement process also explains the electrochemical observation that the oxidation of $[\text{NiL}]^{2+}$ even in sulphate media is irreversible.

(b) *Oxidation of $[\text{NiL}]^{2+}$ by hydroxyl radicals.* N₂O-saturated solutions containing $(1-10) \times 10^{-4} \text{ mol dm}^{-3} [\text{NiL}^{3+}][\text{ClO}_4]_2$ at pH 3.3 were irradiated. The formation of a short-lived intermediate, the spectrum of which is plotted in Figure 4, was observed. The rate constant for the reaction, $(4.0 \pm 0.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, was calculated from the results. The short lived $[\text{NiL}^{3+}]^{3+}$ thus formed decays in two consecutive first-order processes with $k = (5.0 \pm 0.5) \times 10^4 \text{ s}^{-1}$ and $k = 0.33 \pm 0.06 \text{ s}^{-1}$ respectively. The first process causes a decrease in the absorption coefficients without a significant change in the spectral features and is attributed to a rearrangement (configurational isomerization) of the tervalent nickel complex. The second process causes a bleaching of the absorption bands due to the tervalent nickel complex and is therefore attributed to its decomposition.

When the experiments are repeated in solutions containing 0.1 mol dm⁻³ Na₂SO₄ similar results are obtained. The spectra of the transients, Figure 4, and the rates of their formation and decomposition are identical within experimental accuracy to those observed in the absence of sulphate. (The rate of the last step is $0.14 \pm 0.02 \text{ s}^{-1}$ instead of 0.33 s^{-1} .) Thus under these conditions sulphate does not co-ordinate to the tervalent nickel prior to its decomposition. As the electrochemical results indicate that sulphate stabilizes $[\text{NiL}^{3+}]^{3+}$ even at pH 6.0, Figure 3, the explanation of the pulse radiolysis observations has to originate from kinetic barriers to the formation of $[\text{NiL}^3(\text{SO}_4)]^+$. It should be pointed out that the difference between the two techniques stems from the fact that the hydroxyl free radicals, formed in the pulse radiolysis experiments, are powerful one-electron oxidizing reagents and therefore the free energy gain in reaction (1) is so large that the reaction occurs without prior isomerization of the nickel complex. On the other hand, the electrochemical oxidation

occurs at a potential only slightly more positive than the thermodynamic redox potential. Therefore, when the tervalent complex has a configuration which differs considerably from that of the divalent complex, the electrochemical oxidation is not reversible.

Conclusions

The Table summarizes the redox potentials and half-lives of different saturated tetra-aza macrocyclic complexes of tervalent nickel in acidic perchlorate and sulphate solutions. The results clearly indicate that neither the redox potentials nor the half-lives are directly correlated to the size of the cavity of the macrocyclic ligand. Both these values are also not correlated to λ_{max} of $[\text{NiL}]^{2+}$ in nitromethane, *i.e.* to the ligand-field strength of the ligand.¹⁶ In this respect the properties of the tervalent nickel complexes differ from those of the corresponding monovalent complexes, Table.¹⁷⁻¹⁹

The stability constants for sulphate ligation to the tervalent nickel complexes, as deduced from the difference in the redox potentials of the complexes in perchlorate and sulphate containing solutions, are not directly related to any other property of the complexes. The effect of sulphate ligation on the half-lives of the complexes is not related to either the redox potentials of the complexes or the stability constants for sulphate ligation.

All these observations seem to stem from the fact that whereas the divalent nickel complexes are planar the tervalent complexes are octahedral⁹ or five-co-ordinated,⁹ and due to the higher charge their redox potential depends on stabilization *via* solvation. Thus the detailed conformation of the macrocyclic ligand affects its redox potential and capacity to bind sulphate. All these factors are less important for the reduction of the divalent to the corresponding monovalent complexes as the latter, due to the weak acidity of the monovalent nickel cation, require little stabilization *via* axial co-ordination of solvation.

Finally the mechanism of decomposition of the tervalent nickel complexes in aqueous solutions involves the introduction of carbon-nitrogen double bonds into the macrocyclic ligand.^{6,8} The rate of the process seems to require a specific orientation of the protons bound to the carbon atoms adjacent to the nitrogen atoms and therefore the specific rates of these processes depend strongly on the detailed structure of the macrocyclic ligand and the presence or absence of axial ligands, *e.g.* sulphate. The observations in this respect reported here are in full agreement with earlier suggestions.⁹

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