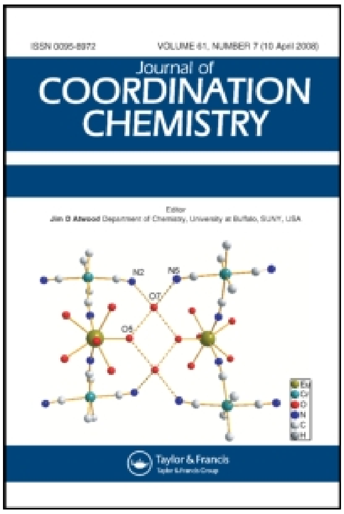

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SPECTRAL CHARACTERISTICS AND KINETIC FEATURES OF REDOX REACTIONS OF NICKEL(II) AND NICKEL(III) COMPLEXES WITH DIOXOTETRAAZA MACROCYCLIC LIGANDS

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Spectral characteristics of nickel(II) and nickel(III) complexes with unsubstituted and benzyl-substituted 13- and 14-membered dioxotetraaza macrocyclic ligands have been studied. The interaction of nickel(II) complexes with peroxodisulfate was shown to yield two different products depending on the ring size of the macrocycle: $[Ni(III)L]^+$ in case of 14-membered ligands and NiL_{-2H}, *i.e.* nickel(II) complexes with the oxidized macrocycle, in case of 13-membered ligands. The $[Ni(III)L]^+$ complexes decompose in neutral solutions *via* an intramolecular redox reaction to yield $Ni(II)L_{-2H}$ compounds. The presence of a new C=N bond in the products of redox reaction was established by means of electronic spectroscopy and ^1H and ^{13}C NMR data. Rate constants and activation parameters for oxidation of Ni(II)L by peroxodisulfate and decomposition reactions of $[Ni(III)L]^+$ in aqueous solution at pH 5.7 have also been measured. The influence of ligand structure on the kinetic parameters of redox reactions studied was investigated. Comparison of data obtained with the results of the study of redox reactions of similar copper complexes has been made and possible reaction mechanisms discussed.

Keywords: Nickel(II,III), dioxotetraazamacrocycles, spectra, redox, kinetics

INTRODUCTION

The chemistry of 3d transition metals in unusually high oxidation states is of great current interest. It has been found that neutral tetraazamacrocyclic ligands can effectively stabilize the nickel(III) ion in acidic aqueous solution, although the complexes are much less stable in neutral and alkaline media.[1,2] On the other hand, saturated tetraazamacrocycles containing only secondary amine donors do not stabilize copper(III). It was established recently that macrocyclic ligands containing both amine and deprotonated amide donor groups also can be used to obtain stable complexes with highly oxidized metal ions, especially copper(III) and nickel(III).[3,4] The stabilizing effect of amide groups has been shown formerly in the cases of nickel(III) and copper(III) complexes with noncyclic polypeptides.[5–7] In spite of a number of reports dealing with the chemical properties of oxoaza macrocyclic complexes, the kinetic characteristics of their redox reactions are practically absent in the literature. Recently we reported some kinetic data concerning the oxidation by peroxodisulfate of copper(II) complexes of the dioxotetraamine macrocyclic ligands H_2L^1–H_2L^4, and the decomposition of the copper(III) complexes which are formed.[8]

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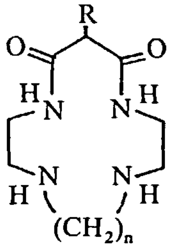


n = 2	R = H	H_2L^1
n = 2	R = CH_2Ph	H_2L^2
n = 3	R = H	H_2L^3
n = 3	R = CH_2Ph	H_2L^4

The purpose of the present work was the investigation of the influence of such ligand structure parameters as ring size and presence of substituents on spectral properties and kinetic behaviour of nickel(II) and nickel(III) complexes with H_2L^1–H_2L^4, and a comparative study of analogous copper compounds, taking into consideration that ligands of this type are ideal for such comparison. The elucidation of the role of the amido *vs* the amino group in determining the properties of nickel complexes was also of interest.

EXPERIMENTAL

Reagents

All reagents used were of reagent grade. Potassium peroxodisulfate was recrystallized twice from water prior to use.

Syntheses

Ligands H_2L^1–H_2L^4 and their nickel(II) complexes were prepared according to literature methods.[3,8,9] Attempts to isolate NiL^2 as a solid, as in the case of CuL^2, were unsuccessful and its solutions were prepared *in situ* by mixing equimolar quantities of the ligand and $Ni(ClO_4)_2{\cdot}6H_2O$, followed by adjustment of pH to 7 with NaOH.

Instrumentation and kinetic measurements

Details concerning physicochemical and kinetic investigations have been described.[8] $^{13}C\ \{^1H\}$ NMR spectra at 22.66 MHz have been obtained using CXP-90 (Bruker) spectrometer in D_2O at ambient temperatures with acetone as internal standard ($\delta(CH_3)$ 30.2 ppm). All kinetic measurements, unless otherwise stated, were carried out at an ionic strength $I = 0.1$ M ($NaClO_4$). The observed rate constants were measured with a precision of about 10%. Accuracy of activation parameter measurements is about 5 kJ mol^{-1} for $\Delta H^{\neq}$ and 10 J mol^{-1} K^{-1} for $\Delta S^{\neq}$.

RESULTS AND DISCUSSION

Properties of nickel(II) complexes

The properties of nickel(II) complexes with dioxotetraaza macrocyclic ligands differ considerably in several respects from those of the widely studied complexes with neutral polyamine macrocycles. The first concerns their inclination towards dissociation in solution. While the latter are extremely stable in aqueous solutions at all pH values, the former undergo rapid dissociation in acid.

$$\mathrm{NiL} + 2\mathrm{H}^+ \rightleftharpoons \mathrm{Ni_{aq}}^{2+} + \mathrm{H_2L} \qquad (1)$$

The equilibrium (*1*) is almost completely shifted to the left at pH > 7 for complexes with 13-membered ligands and pH > 6.5 for complexes with 14-membered ligands.[4] The dissociation rate is proportional to the square of the hydrogen ion concentration and thus increases rapidly as the pH of the solution decreases ($k_{diss} = 1.23 \times 10^5$ $M^{-2} s^{-1}$ for NiL^3).[10]

Another difference due to the presence in the ligand molecule of two deprotonated amide groups is the negligible (<2%) amount of the six-coordinate high-spin form of these complexes in aqueous solution, in contrast to complexes with [13]aneN_4 and [14]aneN_4, where the content of the high-spin form equals 13 and 29%, respectively.[11]

The d–d transition energy in nickel(II) complexes is more sensitive to macrocycle ring size than in similar copper(II) compounds. A considerable increase in equatorial ligand field strength in complexes with 13-membered ligands as compared to 14-membered ones is observed (Table I), in agreement with the general trend characteristic of square-planar nickel(II) complexes (d–d absorption maxima for Ni([13]aneN_4)$^{2+}$ and Ni([14]aneN_4)$^{2+}$ are located at 23,500 and 22,500 cm^{-1}, respectively).[4,12]

TABLE I
Spectral characteristics of the nickel(II) complexes.

Complex	$\nu_{C=O}$, cm^{-1}	Absorption maxima,[a] cm^{-1}		
NiL^1	1560	24000(79)	41400 sh(6500)	47300(19000)
NiL^2		23800(60)	40000 sh(3700)	47000(19200)
NiL^3	1580	21700(74)	40800 sh(6000)	46600(20900)
NiL^4	1580	21900(66)	40000 sh(4900)	47400(21100)

[a] Aqueous solution; sh, shoulder; extinction coefficients ($M^{-1} cm^{-1}$) are given in parentheses.

It should be noted that the replacement of two amine groups by two amides causes a slight increase in d–d transition energy for the complexes with 13-membered ligands and a decrease for 14-membered complexes. This may be due, in our opinion, to the fact that the presence of a planar six-membered deprotonated diamide chelate ring in the coordinated macrocycle makes the ligand structure more rigid, leading to the deviation of the amine donor atoms from optimal positions in the coordination sphere. This effect can be destabilizing in the case of 14-membered ligands which fit the nickel(II) ion better than do 13-membered analogues. However, this problem needs additional investigation since, in contrast to polyamine complexes, d–d transition bands in the compounds under consideration are unsymmetric; a direct comparison of ligand field strength based on the position of absorption maxima may be not entirely correct.

UV absorption bands in nickel(II) complexes with H_2L^1–H_2L^4 appear in the same region as in complexes with the amine macrocycles, but a shoulder on the low-energy tail of this band is indicative of the amide-containing ligands.

Cyclic voltammograms of NiL^1–NiL^4 measured in aqueous 0.1 M $NaClO_4$ are poorly reversible, but at higher ionic strength they become *quasi*-reversible. In 3 M $NaClO_4$ solution, $E_{1/2}$ values for $[NiL^1]^{+/0}$ and $[NiL^3]^{+/0}$ are equal to 0.91 and 0.85 V *vs* SCE, respectively.[13] In contrast to copper complexes with the same ligands, an increase in macrocycle ring size from 13 to 14 in the nickel compounds leads to a decrease of redox potential value (*i.e.* higher thermodynamic stabilization of nickel (III) in a complex with a 14-membered ligand). This is due to the fact that the metal–donor atom distance (d) for nickel(III) ion is greater than for the low-spin nickel(II) ion, d(Ni(III)–N) > d(Ni(II)–N), but for copper d(Cu(III)–N) < d(Cu(II)–N).[4,13]

Comparison with polyamine macrocyclic nickel complexes is more difficult since most data concerning such complexes have been obtained in acidic solution containing rather high sulfate concentrations, conditions known to stabilize nickel(III) in this case. For example, $E_{1/2}$ values for $Ni([13]aneN_4)^{3+/2+}$ and $Ni([14]aneN_4)^{3+/2+}$ in neutral 0.5 M Na_2SO_4 solution are equal to 0.65 and 0.45 V *vs* SCE respectively,[14,15] but in neutral 0.1 M $NaClO_4$ solution the value for $Ni([14]aneN_4)^{3+/2+}$ is considerably higher, 0.74 V.[16] On the other hand, any stabilizing effect of sulfate is practically absent for NiL^1 and NiL^3 (in 0.5 M Na_2SO_4, $E_{1/2}$ values are 0.90 and 0.81 V *vs* SCE, respectively).[17] In contrast to copper complexes, where introduction of the amide group in the ligand causes a drastic potential decrease, this is not the case for nickel compounds.

Spectral characteristics of nickel(III) compounds and products of their redox decomposition

Potassium peroxodisulfate was used to generate nickel(III) complexes in solution. The behaviour of NiL^3 and NiL^4 (14-membered ligands) differs considerably from that of complexes with 13-membered ligands. In the first case, after addition of the oxidant to the nickel(II) complex solution, an intense absorption in the UV and visible spectral regions appears and persists for several minutes. Disappearance of this product is accompanied by the formation of a new band of much lower intensity having a maximum at 34,000 cm^{-1} (Fig. 1A). When the reaction was carried out in buffer solutions (phosphate, acetate, TRIS) short-lived products were not detected in any significant amount and only the absorption growth at 34,000 cm^{-1} was observed. Slow electrochemical oxidation of NiL^3 or NiL^4 (with or without buffer) leads to the same result.

Intensely coloured products have not been detected during oxidation of NiL^1 or NiL^2 in any case; only the appearance and growth of absorption in UV region with a maximum at about 33,000 cm^{-1} was observed (Fig. 1B).

To record the absorption spectra of the products formed in the initial stages of peroxodisulfate oxidation of NiL^3 and NiL^4, the fact was used that addition of acid to the solution containing Ni(II)L causes, as mentioned above, its rapid dissociation. $[Ni(III)L]^+$ compounds are much more resistant to the action of acid. The spectra of $[Ni(III)L]^+$ compounds obtained in such a way are characterized by broad bands with maxima at 34,000 cm^{-1} and a shoulder at *ca* 28,000 cm^{-1}. Extinction coefficients at the maxima were determined in the same way as for copper(III) compounds[8] by titration of acidic solutions with $K_4Fe(CN)_6$ and the values are 14,800 ± 300 and 12,300 ± 300 M^{-1} cm^{-1} for $[Ni(III)L^3]^+$ and $[Ni(III)L^4]^+$, respectively.

Assignment of these spectra to nickel(III) complexes is supported by the fact of their disappearance on addition of reductants and by ESR spectroscopy. ESR spectra are typical of the low-spin d^7 electronic configuration in a tetragonally distorted environment ($g_{\parallel} = 2.020$, $g_{\perp} = 2.250$ for $[Ni(III)L^3]^+$ and $g_{\parallel} = 2.022$, $g_{\perp} = 2.245$ for $[Ni(III)L^4]^+$ in acid).

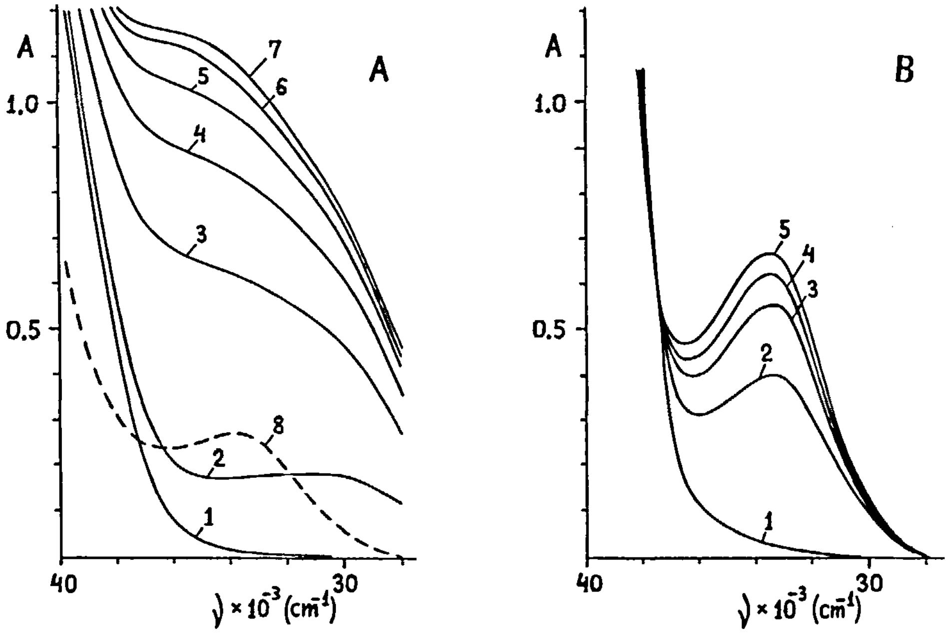


FIGURE 1 Spectral changes observed during oxidation of NiL^3 (A) and NiL^1 (B) by peroxodisulfate. Concentrations: A—$[NiL^3] = 4.69 \times 10^{-4}$ M, $[S_2O_8^{2-}] = 2.35 \times 10^{-4}$ M ($l = 0.5$ cm); B—$[NiL^1] = 9.38 \times 10^{-4}$ M, $[S_2O_8^{2-}] = 2.50 \times 10^{-4}$ M ($l = 1.0$ cm). Time intervals: A—1.5 min (spectrum 8 was recorded 50 min after spectrum 7); B—2 min.

The electronic spectra observed do not depend much on the nature of the acid used ($HClO_4$, H_2SO_4, H_3PO_4), so the nickel(III) complexes are present in solution probably as aqua compounds, $[Ni(III)L(H_2O)_2]^+$, without coordination of anions in axial positions. The same effect was observed also for nickel(III) complexes with noncyclic polypeptides.[18]

Spectral characteristics of compounds formed as a result of $[Ni(III)L^3]^+$ and $[Ni(III)L^4]^+$ decomposition are similar to those of compounds obtained during oxidation of NiL^1 and NiL^2. The absorption bands at 34,000 cm^{-1} (or 33,000 cm^{-1} for complexes with 13-membered ligands) do not disappear upon addition of reductants. All these compounds are diamagnetic in solution and their ^1H and ^{13}C NMR spectra have been measured (Fig. 2).

On the basis of the experimental results, the conclusion can be drawn that these compounds are the nickel(II) complexes NiL_{-2H}, where L_{-2H}^{2-} is the oxidized form of the macrocyclic ligand. ^{13}C NMR data show, along with a number of new signals in the CH_2 region, signals at 173.9 ppm for $NiL^1{}_{-2H}$ and 178.1 ppm for

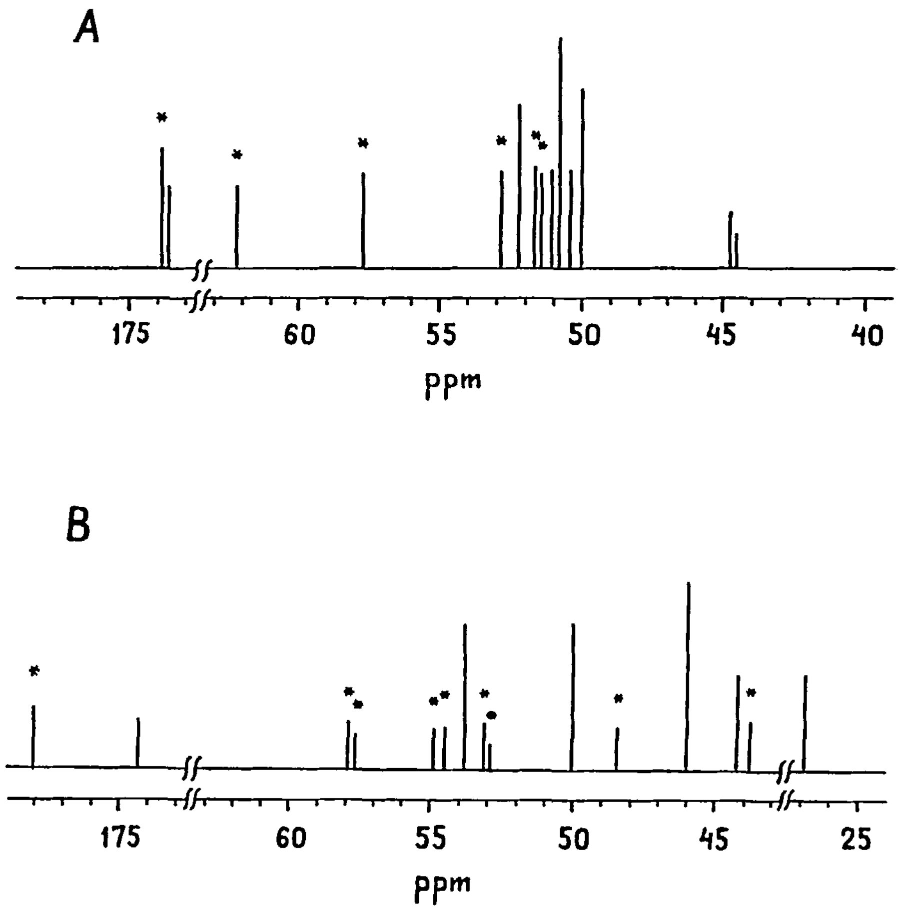
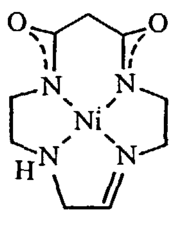
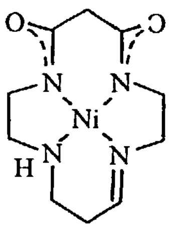


FIGURE 2 ^{13}C NMR spectra of the reaction mixture obtained after oxidation by peroxodisulfate of NiL^1 (A) and NiL^3 (B); new signals which are absent in the spectra of starting complexes are marked with asterisk.

NiL^3_{-2H} (typical of azomethine carbons). This assignment was supported by coupling constant measurements. Further proof is the appearance of signals at *ca* 7.8 ppm in the PMR spectra, which are also indicative of the -CH=N-group. The following structures are, in our opinion, most probable for NiL_{-2H}, taking into account the relatively great difference between the positions of the azomethine carbon signals in the ^{13}C NMR spectra.





The NiL_{-2H} complexes are rather stable in neutral solution, but addition of acid causes their dissociation and relatively rapid hydrolysis of the protonated ligands at the azomethine bond (*ca* 3 h in 5×10^{-2} M $HClO_4$ at room temperature).

Extinction coefficients of the UV absorption bands of NiL_{-2H} complexes have been estimated using values of maximum absorbance achieved under reaction conditions, when an excess of NiL over peroxodisulfate was used, and assuming that one molecule of the two-electron oxidant $K_2S_2O_8$ is consumed per C=N bond formed (it should be noted that under such conditions an isosbestic point in the spectra has been observed during oxidation). The ε values obtained in this way lie in the range 2300–2400 $M^{-1}\,cm^{-1}$ and are in good agreement with data for nickel(II) complexes with macrocyclic ligands containing one azomethine bond (*e.g.* for $Ni(Me_3[14]\text{-}eneN_4)^{2+}$ $\varepsilon = 2000\,M^{-1}\,cm^{-1}$ for a band with $\nu_{max} = 37{,}000\,cm^{-1}$).[16]

The NiL_{-2H} complexes can be oxidized further when, for example, higher $S_2O_8{}^{2-}$ concentrations are used. In this case the isosbestic point does not hold for the later reaction stages and additional absorption growth is accompanied by a slight ($\sim 1000\,cm^{-1}$) bathochromic shift of the band maximum. The ε values estimated in a similar way are approximately two times greater than for NiL_{-2H}, so that formation of a second C=N bond can be assumed.

Spectral changes in the visible region observed in the course of oxidation of NiL are also in agreement with C=N bond formation since the energy of the d–d transition in oxidation products increases because of the higher ligand field provided by azomethine donor groups as compared to amines.[12]

Kinetics of oxidation of nickel(II) complexes by peroxodisulfate

Interaction of nickel(II) complexes with peroxodisulfate leads in the initial stages of reaction to two different products depending on the ring size of the macrocycle as described above. The following scheme can be used to describe the processes observed.[19]

$$Ni(II)L + S_2O_8{}^{2-} \overset{K_{eq}}{\rightleftharpoons} [Ni(II)L\,|\,S_2O_8{}^{2-}] \qquad (2)$$

$$[Ni(II)L\,|\,S_2O_8{}^{2-}] \xrightarrow{k_{et}} [Ni(III)L]^+ + SO_4{}^{2-} + SO_4{}^{\dot{-}} \qquad (3)$$

$$Ni(II)L + SO_4{}^{\dot{-}} \xrightarrow{fast} [Ni(III)L]^+ + SO_4{}^{2-} \qquad (4)$$

$$[Ni(III)L]^+ \xrightarrow{k_{redox}} Ni(II)L_{-2H} + 2H^+ \qquad (5)$$

The process (*5*) is complex and includes several elementary steps.

Rate constants for the oxidations were determined from the initially linear regions of the kinetic curves for product formation. In all cases the reaction was first-order in both reagents and effective rate constants, k_{eff}, were calculated for (*6*),

$$k_{eff} = (dA_p/dt)_0/\varepsilon_p l[NiL]_0[S_2O_8{}^{2-}]_0 \qquad (6)$$

where A_p is the absorption due to the product, ε_p is its extinction coefficient and l is optical path length. Activation parameters have been determined from the temperature dependence of k_{eff} in the temperature intervals 25–50°C for oxidation of NiL^1 and NiL^2 and 6–25°C for oxidation of NiL^3 and NiL^4 (Table II).

To confirm that the nickel(II) to nickel(III) oxidation is rate-limiting in all cases independent of the reaction products, oxidation kinetics of NiL^3 in phosphate buffer at higher temperature (40–56°C) have been studied, *i.e.*, under conditions when only $NiL^3{}_{-2H}$ is formed in solution. Activation parameters thus obtained for this reaction ($\Delta H^{\neq} = 24\,kJ\,mol^{-1}$, $\Delta S^{\neq} = -139\,J\,mol^{-1}\,K^{-1}$) are in excellent agreement with values derived from the study of nickel(III) complex formation (Table II). These data lead us to believe that the kinetic parameters obtained for oxidation of nickel(II) complexes with 13-membered ligands are truly characteristic of a nickel(II) to nickel(III) process. It should be noted that effective rate constants $k_{eff} = 2\,K_{eq}\,k_{et}$. This means that the activation parameters obtained should reflect both the electron transfer step (*3*) and the equilibrium (*2*).

TABLE II
Kinetic parameters for oxidation reactions of nickel(II) complexes by peroxodisulfate (0.1 M $NaClO_4$, 298 K).

Complex	k_{eff}, $M^{-1}\,s^{-1}$	$\Delta H^{\neq}$, $kJ\,mol^{-1}$	$\Delta S^{\neq}$, $J\,mol^{-1}\,K^{-1}$
NiL^1	13.0[a]	32	−111
NiL^2	1.7[a]	41	−104
NiL^3	8.1	25	−142
NiL^4	2.9	32	−130

[a] An ε_p value of $2350\,M^{-1}\,cm^{-1}$ was used for calculations.

It follows from Table II that rather distinct tendencies exist in variations of kinetic parameters as a function of ligand structure. The presence in the ligand molecule of the benzyl substituent leads to lower effective rate constants and more positive $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values. An increase of ring size in the macrocycle causes a substantial lowering of activation enthalpies and makes activation entropies more negative. It is interesting to note that similar trends have been observed in the oxidations of copper(II) complexes with the same ligands.[8] This may be connected to a similar influence of structural factors on the transition state in both processes. In general, nickel(II) complexes NiL^1–NiL^4 are oxidized to nickel(III) compounds by peroxodisulfate substantially (10 to 100 times) faster than analogous copper complexes, the $\Delta H^{\neq}$ values in the latter case being considerably (10 to 20 kJ mol^{-1}) higher and $\Delta S^{\neq}$ values being more positive (20 to 30 J mol^{-1} K^{-1}).[8]

Oxidations of nickel(II) complexes with neutral 14-membered tetraaza ligands in comparison to the complexes studied are also characterized by similar kinetic features.[19] For example, in weak acidic solution (pH 4, 0.1 M $NaClO_4$) k_{eff} for $Ni([14]aneN_4)^{2+}$ oxidation by $S_2O_8{}^{2-}$ equals $4.5\,M^{-1}\,s^{-1}$ at 25°C with $\Delta H^{\neq} = 39$ $kJ\,mol^{-1}$ and $\Delta S^{\neq} = -92\,J\,mol^{-1}\,K^{-1}$.[20]

The differences observed in oxidations of nickel and copper complexes can probably be explained to a certain degree by the fact that equilibrium (*7*) really exists in solutions of copper complexes, rather than (*2*).

$$ML(H_2O)_n + S_2O_8^{2-} \overset{K_{eq}}{\rightleftharpoons} [ML(H_2O)_{n-1}S_2O_8^{2-}] + H_2O \qquad (7)$$

The same considerations may also be applicable to the reactions of nickel complexes with polyamine ligands since considerable amounts of the high-spin six-coordinate form are present in solution in this case, although direct comparison of kinetic parameters is not entirely correct because of different influences of electrostatic factors on equilibria (*2*) and (*7*).

Kinetics of decomposition of nickel(III) complexes

The nickel(III) complexes are relatively unstable in neutral aqueous solution. Electron transfer from the coordinated amine nitrogen atom of the macrocycle to the nickel(III) ion, which is accompanied by proton release, seems to be a rate-limiting step for the nickel(III) decomposition. The nickel(II) complex with the ligand radical undergoes further oxidation by $[Ni(III)L]^+$, $SO_4^{\dot{-}}$ or $S_2O_8^{2-}$ to yield a compound of the oxidized ligand containing the C=N bond. Buffers, when present, catalyse this process effectively. The reason for such behaviour lies, in our opinion, in the ability of weak acid anions to promote amine proton dissociation (it should be noted that phosphoric acid, for example, does not accelerate the decomposition of the nickel(III) complexes in comparison to other acids, so that the destabilizing effect of the phosphate buffer is due to phosphate anions only).

Since the formation of measurable amounts of nickel(III) complexes with 13-membered ligands has not been observed in our experiments, their kinetic stability was estimated on the basis of known oxidation rate constants and expected approximate values of $[Ni(III)L]^+$ extinction coefficients. The half-life of these compounds does not exceed several tenths of a second, *i.e.*, it is at least three orders of magnitude lower than that of nickel(III) complexes with 14-membered ligands. This is in agreement with the redox potentials of the complexes studied, although the much greater difference in kinetic stability between complexes of 13- and 14-membered ligands in the case of nickel(III) as compared with copper(III)[8] should be emphasized.

Decompositions of nickel(III) complexes with H_2L^3 and H_2L^4 in aqueous solution at pH 5.7 were found to be in agreement with (*8*).

$$-d[Ni(III)L]/dt = k_d[Ni(III)L] \qquad (8)$$

Activation parameters for these processes have been calculated from temperature dependences of k_d in the regions 25–46°C for $[Ni(III)L^3]^+$ and 17–34°C for $[Ni(III)L^4]^+$ (Table III).

TABLE III

Kinetic parameters for decomposition reactions of nickel(III) complexes (0.1 M $NaClO_4$, 298 K, pH 5.7).

Complex	k_d, s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
$[NiL^1]^+$	>10		
$[NiL^2]^+$	>10		
$[NiL^3]^+$	4.5×10^{-3}	65	−73
$[NiL^4]^+$	5.4×10^{-3}	46	−132

Although rate constants for $[Ni(III)L^3]^+$ and $[Ni(III)L^4]^+$ are very similar, it is seen from Table III that activation parameters differ considerably. As for copper(III),[8] the reaction of the benzyl-substituted complex is characterized by lower $\Delta H^{\neq}$ and more negative $\Delta S^{\neq}$ values and variation of activation parameters as a function of ligand structure is opposite to that observed for oxidation processes (Table II).

The similar effect of the benzyl group on the activation parameters for decompositions both of copper and nickel complexes allows us to suppose that this substituent has little influence on solvation/desolvation when the oxidation state of the metal ion is changed from +3 to +2 (these processes are conjugated with coordination of water molecule(s) by copper and release of water molecules by nickel).

In general, the nickel(III) complexes under consideration are much less stable in neutral solution than comparable copper(III) compounds.[8] On the other hand $[Ni([14]aneN_4)(H_2O)_2]^{3+}$ is more kinetically stable under similar conditions, although half-lives of nickel(III) complexes with some methyl-substituted derivatives of $[14]aneN_4$ are of the order of only a few seconds.[20] As noted above, the kinetic stability of nickel(III) complexes wth dioxotetraamine macrocycles increases in acids strongly and in some cases is greater than that of $Ni([14]aneN_4)^{3+}$ (in 0.1 M $HClO_4$ $k_{obs} = 9.8 \times 10^{-6}\,s^{-1}$ for $[Ni(III)L^3]^+$ and $3.0 \times 10^{-5}\,s^{-1}$ for $Ni([14]aneN_4)^{3+}$).[20]

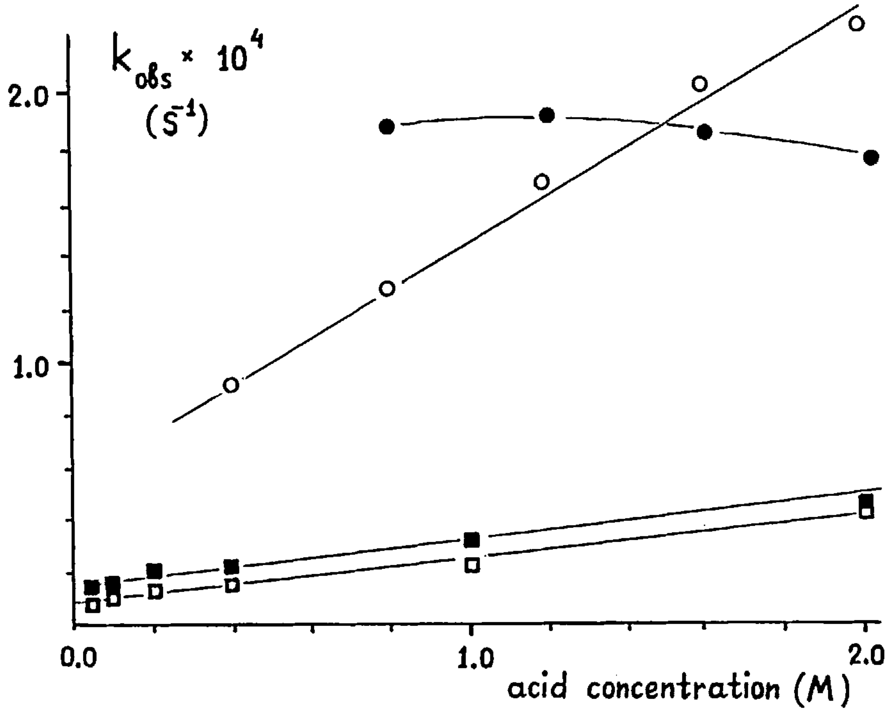


FIGURE 3 Plots of k_{obs} *vs* acid concentration for decomposition reactions of $[Ni(III)L^3]^+$ (□) and $[Ni(III)L^4]^+$ (○) in perchloric (open symbols) and sulfuric (solid symbols) acid.

The main difference between these two types of complexes concerns the stabilizing effect of highly charged anions like sulfate, phosphate and so on, which is very substantial for the complexes with neutral ligands and is practically absent for $[Ni(III)L^3]^+$ and $[Ni(III)L^4]^+$ (Fig. 3). This is probably due to the fact that the high positive charge of nickel(III) ion is compensated to a great extent by the negative charge of the two deprotonated amide groups and no or little additional coordination of anions occurs.

As follows from Figure 3, an increase of acid concentration leads to the acceleration of nickel(III) complex decomposition (except for $[Ni(III)L^4]^+$ in sulfuric acid). Linear plots of k_{obs} *vs* acid concentration give the dependence (*9*),

$$k_{obs} = k_0 + k_H [H^+] \tag{9}$$

with $k_0 = 2 \times 10^{-5} s^{-1}$ and $6 \times 10^{-5} s^{-1}$ for reactions of $[Ni(III)L^3]^+$ and $[Ni(III)^4]^+$, respectively (in $HClO_4$). The presence of the $k_H [H^+]$ term in (*9*) suggests that this process proceeds *via* protonation of the nickel(III) complexes (apparently at the oxygen atom of the amide group).[21]

The data obtained show that some differences exist for mechanisms of decomposition of nickel(III) and copper(III) complexes with dioxotetraamines in acidic media; for the latter, the pH-independent term k_0 is absent.[8] A much greater kinetic stability of nickel(III) complexes with 14-membered ligands in acidic solutions in comparison to analogous copper(III) compounds should also be noted. For example, k_{obs} for $[M(III)L^3]^+$ in 0.1 M $HClO_4$ is equal to $9.8 \times 10^{-6} s^{-1}$ and $6.0 \times 10^{-3} s^{-1}$ for nickel(III) and copper(III) complexes, respectively. At present, however, details of mechanism for nickel(III) complex decomposition leading to the differences observed for $[Ni(III)L^3]^+$ and $[Ni(III)L^4]^+$ in sulfuric and perchloric acid solutions are not clear and require further investigation.

CONCLUSIONS

The data obtained show that the structure of the dioxotetraaza macrocyclic ligands in nickel complexes plays a dominant role in determining both their spectral and redox properties. Analysis of kinetic data shows that the first stage in peroxodisulfate oxidation of all nickel(II) complexes studied is the formation of nickel(III) compounds. The kinetic stability of the nickel(III) complexes in neutral solutions depends strongly on the macrocycle ring size and correlates well with thermodynamic data (*i.e.* redox potential of the $[NiL]^{+/0}$ pair). For the relatively unstable complexes of 13-membered ligands having higher $E_{1/2}$ values, the only product seen is the nickel(II) complex of the oxidized macrocycle containing a new azomethine bond. Complexes of nickel(III) with 14-membered ligands and kinetically more stable, but also decompose *via* intramolecular electron transfer to yield, as in the former case, nickel(II) complexes with oxidized ligands.

Changes in activation parameters for the redox reactions studied as a function of ligand structure resemble those for related copper compounds but the nickel(II) complexes are oxidized much more rapidly, probably reflecting the absence of coordinated axial water molecules in NiL in contrast to CuL. Nickel(III) complexes are kinetically less stable in neutral solution as compared to copper(III). In acidic solution, the kinetic stability of nickel(III) compounds is much higher than of copper(III) species despite the more positive redox potentials of the former. This may be connected with inherent features of the reaction mechanisms in both cases, so far as the dependence of the observed rate constants for decomposition on acid concentration differ significantly for $[Ni(III)L]^+$ and $[Cu(III)L]^+$.

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