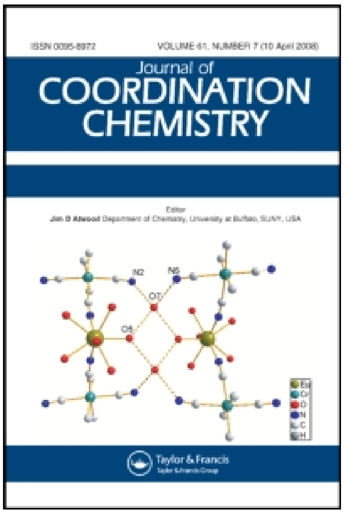

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KINETICS OF PEROXODISULFATE OXIDATION OF BIS(MACROCYCLIC) DINICKEL(II) COMPLEXES: THE ROLE OF THE COORDINATION NUMBER OF THE METAL ION

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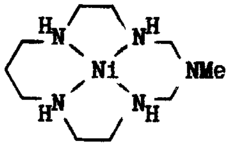
Kinetics of peroxodisulfate oxidation of a number of homologous bis(macrocyclic) dinickel(II) complexes in weakly acidic solutions (pH~6) does not depend on ligand structure and resembles that of their 14-membered monomacrocyclic analogue. By contrast, parameters obtained in 0.1 M H_2SO_4 show marked differences depending on the lengths of plymethylene chains connecting two mono-macrocyclic subunits. Such behaviour is explained by the distinct reactivity of different forms of complexes (*i.e.*, four- or six-coordinated) prevailing in solution, with the square-planar form being more reactive. No evidence to suggest the complementary two-electron oxidation of dinickel(II) complexes by peroxodisulfate was obtained.

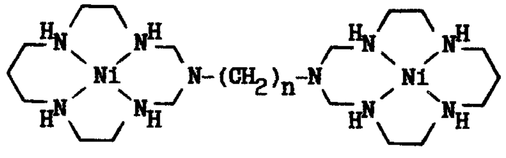
KEYWORDS: Bis(macrocyclic) complexes, nickel(II,III), redox reactions, kinetics, activation parameters

INTRODUCTION

The study of the chemical behaviour of polynuclear coordination compounds is a subject of much current interest from the viewpoint of estimation of factors which determine the properties and reactivity of such systems with respect to catalytic and biochemical processes. Recently, we described the synthesis and some properties of a homologous series of bis(macrocyclic) dinickel complexes of general formula Ni_2LX^{4+} consisting of two equivalent pentaaza macrocyclic subunits (NiL1) linked by aliphatic chains of different lengths.[1,2]



$NiL1^{2+}$



Ni_2LX^{4+} X = n n = 2,3,4,5

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It was shown that spectroscopic characteristics of both dinickel(II) and dinickel(III) compounds, as well as Ni^{III}/Ni^{II} potentials are very close to corresponding parameters of their monomacrocyclic analogue NiL1. This clearly indicates the lack of intramolecular metal-metal interactions in dinickel complexes of this type.[1,2]

It has been formerly demonstrated with a great number of nickel(II) tetraazamacrocyclic complexes that the presence of methyl substituents in the macrocyclic backbone creating steric hindrance for interactions with an oxidant exerts an determining influence on kinetic parameters of oxidation to nickel(III) compounds by peroxodisulfate.[3] Bis(macrocyclic) complexes Ni_2LX^{4+} do not contain any substituents which are able to suppress such a redox interaction. However, preliminary experiments have shown that kinetics of oxidation by $S_2O_8^{2-}$ depends substantially on the length of the connecting chain between macrocyclic subunits.[1] The aim of present work was a more detailed study of the peculiarities of above-mentioned redox reactions in comparison with their monomacrocyclic analogue to elucidate factors introduced in such processes by the binuclear nature of the reductants.

EXPERIMENTAL

All reagents, instrumentation and kinetic techniques have been described.[3–5] Mono- and bis(macrocyclic) nickel(II) complexes as perchlorates were synthesized according to the literature.[1,2] The kinetics of formation of nickel(III) complexes was followed spectrophotometrically (λ_{max} = 312 nm). The value of the molar absorption coefficient ε at this wavelength was taken to be 11,000 M^{-1} cm^{-1} per macrocyclic nickel(III) ion.[1,2] The observed rate constants were measured with a precision of about 10%. Activation parameters ($\Delta H^{\neq} \pm 5$ kJ mol^{-1} and $\Delta S^{\neq} \pm 10$ J mol^{-1} K^{-1}) were calculated from the temperature dependence (16–60°C) of observed rate constants.

RESULTS AND DISCUSSION

The interaction of mono- and bis(macrocyclic) nickel(II) complexes with peroxodisulfate ions in sulfate-containing solutions leads to formation of compounds with practically identical spectral characteristics typical of low-spin tetragonal hexacoordinated nickel(III) with sulfate ions in axial positions.[6,7] As oxidation takes place, spectroscopic changes analogous to those observed formerly[3,5] occur — the band at 235 nm disappears simultaneously with a growth of absorbance at 312 nm with an isosbestic point at 260 nm. The stoichiometry of the reactions corresponds to the equation

$$2NiL^{2+} + S_2O_8^{2-} = 2NiL^{3+} + 2SO_4^{2-} \qquad (1)$$

where [NiL] = [NiL1] or 1/2 [Ni_2LX] (axially coordinated ligands in nickel complexes are omitted for simplicity).

Taking into account literature data,[3,4,8] processes involved with oxidation of the bis(macrocyclic) nickel(II) complexes can be represented as follows

$$\mathrm{Ni_2^{II}LX^{4+} + S_2O_8^{2-} \xrightleftharpoons{K_{IP}} \{Ni_2^{II}LX,S_2O_8\}^{2+} \xrightarrow{k_{et}} Ni^{II}Ni^{III}LX^{5+} + SO_4^{2-} + SO_4^{-}} \tag{2a}$$

$$\mathrm{Ni^{II}Ni^{III}LX^{5+} + S_2O_8^{2-} \xrightleftharpoons{K'_{IP}} \{Ni^{II}Ni^{III}LX,S_2O_8\}^{3+} \xrightarrow{k'_{et}}}$$

$$\mathrm{Ni_2^{III}LX^{6+} + SO_4^{2-} + SO_4^{\dot{-}}} \tag{2b}$$

$$\mathrm{Ni_2LX^{n+} + SO_4^{\dot{-}} \xrightarrow{fast} Ni_2LX^{(n+1)+} + SO_4^{2-} (n = 4 \text{ or } 5)} \tag{2c}$$

$$\mathrm{Ni_2^{II}LX^{4+} + Ni_2^{III}LX^{6+} \xrightleftharpoons{K_{com}} 2Ni^{II}N^{III}LX^{5+}} \tag{2d}$$

where the rate-limiting step is the electron transfer from nickel(II) to peroxodisulfate characterized by k_{et} and/or k'_{et}. Unfortunately, we are unable to make an estimate of K_{com} and to distinguish whether two-electron oxidation proceeds intramolecularly within one ion pair

$$\mathrm{Ni_2^{II}LX^{4+} + S_2O_8^{2-} \rightleftharpoons \{Ni_2^{II}LX,S_2O_8\}^{2+} \rightarrow Ni_2^{III}LX^{6+} + 2SO_4^{2-}} \tag{3}$$

or *via* sequence (*2a*)–(*2c*) (although this question is intriguing itself), because of following circumstances: (*i*) cyclic voltammograms of dinickel complexes show only one redox transition, *i.e.*, the potentials of $\mathrm{Ni^{II}Ni^{III}LX/Ni_2^{II}LX}$ and $\mathrm{Ni_2^{III}LX/Ni^{II}Ni^{III}LX}$ redox couples differ only slightly, if at all;[1,2] (ii) the bands which might be assigned to intramolecular charge transfer transitions are absent in spectra of oxidation products and at any stage of the reactions the general shape of spectrum is retained and coincides with that of the monomacrocyclic complex.

Thus, we are entitled to use for the description of oxidation processes the following simplified scheme

$$\mathrm{Ni^{II}N_4^{2+} + S_2O_8^{2-} \xrightleftharpoons{K_{IP}} [Ni^{II}N_4,S_2O_8] \xrightarrow{k_{et}} Ni^{III}N_4^{3+} + SO_4^{2-} + SO_4^{\dot{-}}}$$

$$\mathrm{Ni^{II}N_4^{2+} + SO_4^{\dot{-}} \xrightarrow{fast} Ni^{III}N_4^{3+} + SO_4^{2-}} \tag{4}$$

where the nickel ion in the tetraazamacrocyclic environment is symbolyzed by $\mathrm{Ni\ N_4^{n+}}$, irrespective of whether it is in mono- or bis(macrocyclic) compounds and, for the latter, irrespective of oxidation state (+2 or +3) of the neighbouring nickel ion.

The kinetics of oxidation of the nickel(II) complexes obeys the equation

$$\text{rate} = d[\mathrm{Ni^{III}L}]/dt = k_{obs}[\mathrm{Ni^{II}L^{2+}}][\mathrm{S_2O_8^{2-}}] \tag{5}$$

and is in good agreement with scheme (*4*), with $k_{obs} = 2K_{IP}k_{et}$. Values of k_{obs} along with activation parameters are collected in Table 1.

The dependence of k_{obs} on ionic strength (Figure 1) is characterized as for other tetraazamacrocyclic nickel(II) compounds[9] by a negative slope and is indicative of interaction in the rate-limiting step of reagents with opposite sign. Moreover, the slope for bis(macrocyclic) complexes is twice as large as that for $\mathrm{NiL1^{2+}}$, in accordance with differences in charges of the compounds under consideration (+2 and +4).[10]

The data presented in Table 1 show higher values of k_{obs} for dinuclear compounds than for $\mathrm{NiL1^{2+}}$, especially in 0.1 M $\mathrm{H_2SO_4}$. To some extent, such differences may be due to electrostatic reasons; since $k_{obs} \sim K_{IP}$, the latter constant,

Table 1 Kinetic parameters for oxidation reactions of nickel(II) complexes by peroxodisulfate in sulfate-containing solutions (295 K).

Complex	Medium[a]	k_{obs}, M^{-1} s^{-1}	$\Delta H^{\neq}_{eff}$, kJ mol^{-1}	$\Delta S^{\neq}_{eff}$, J mol^{-1} K^{-1}
$NiL1^{2+}$	A	0.67	70	-22
	B	4.9	45	-79
Ni_2L2^{4+}	A	12.3	52	-45
	B	13.5	43	-85
Ni_2L3^{4+}	A	13.0	54	-39
	B	13.5	42	-81
Ni_2L4^{4+}	A	7.8	60	-21
	B	16.4	43	-76
Ni_2L5^{4+}	A	4.4	62	-24
	B	17.6	44	-72

[a] A—k_{obs} in 0.1 M H_2SO_4 + 0.187 M $NaClO_4$, activation parameters in 0.1 M H_2SO_4; B—in 0.1 M Na_2SO_4, pH ~ 6.

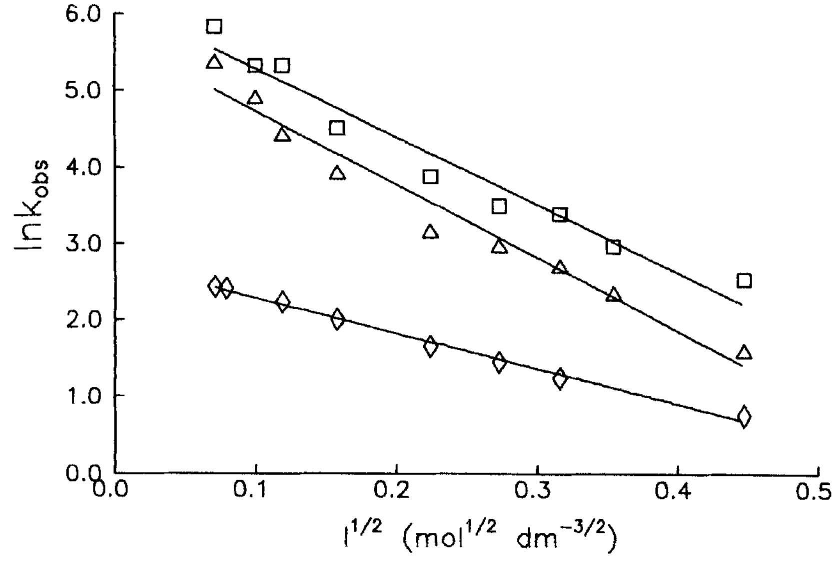

Figure 1 Plot of k_{obs} *versus* ionic strength of solutions containing $NaClO_4$ (pH ~ 6) for the macrocyclic nickel(II) complexes: (□) - $[Ni_2L3]^{4+}$, (△) - $[Ni_2L4]^{4+}$, (◇) - $[NiL1]^{2+}$.

in turn, is proportional to the charges of species forming an ion pair.[11] Unfortunately, numerical calculations of K_{IP} present difficulties in view of the uncertainty in deciding on a model which would describe the shape of bis(macrocyclic) molecules faithfully. Nevertheless, the fact that the dependence of oxidation rate upon $S_2O_8^{2-}$ concentration remains linear even with large concentrations of the oxidant (up to 1000-fold excess relative to nickel(II)) reflects a rather low value of K_{IP}.

The difference in k_{obs} for a given complex in a weakly acidic (0.1 M Na_2SO_4, pH~6) and acidic (0.1 M H_2SO_4) solutions is also worthy of note. This effect manifests itself most for monomacrocyclic complex, whereas for binuclear compounds its progressive diminution is observed with shortening of the connecting chain; at $n \leq 3$ the effect becomes insignificant having regard to the accuracy in determination of k_{obs}.

In our opinion, all above-mentioned kinetic features can be explained by the influence of the coordination number of the nickel(II) ion. It is well documented that four-coordinated square planar, low-spin nickel(II) complexes in solution are inclined to formation of six-coordinated high-spin species[12,13]

$$\mathrm{NiN_4^{ls}} + 2\mathrm{A} \overset{K_{SE}}{\rightleftharpoons} \mathrm{NiN_2A_2^{hs}} \tag{6}$$

with K_{SE} being given by

$$K_{SE} = [\mathrm{NiN_4A_2^{hs}}]/[\mathrm{NiN_4^{ls}}] \tag{7}$$

where superscripts "ls" and "hs" denote low-spin and high-spin, respectively, and A is the solvent molecule or coordinating anion in solution. As a parameter reflecting the equilibrium (*6*), the value of effective molar extinction coefficient, ε_{eff}, corresponding to d–d transition in low-spin form is used (in complexes with 14-membered ligands this band is located at *ca.* 450 nm), since the absorbance of high-spin species at this wavelength is at least one order of magnitude lower.[12] To a first approximation, the decrease of ε_{eff} is proportional to the increasing amount of six-coordinated form in the equilibrium mixture.

As can be seen from Figure 2, the behaviour of binuclear complexes in sulfate media depends on their molecular structure—whereas Ni_2L2^{4+} is practically insensitive to proton concentration, lengthening of the connecting chain between macrocyclic subunits leads to a regular increase of high-spin form at lower pH, with the complex having the longest chain, Ni_2L5^{4+}, being most similar to monomacrocyclic complex. For the latter, such unusual pH-dependent spin equilibrium was shown to be caused by the coordination of hydrogen sulfate to nickel(II), *i.e.*, 2A = HSO_4^- and H_2O in *(6)*.[14]

Taking into account equilibrium (*6*), the rate constant for peroxdisulfate oxidation may be written as

$$k_{obs} = (k^{ls} + k^{hs}K_{SE})/(1 + K_{SE}) \tag{8}$$

and recently we have shown that for $NiL1^{2+}$, $k^{ls} > k^{hs}K_{SE}$.[15]

There is a good reason to believe that the foregoing is valid also for bis(macrocyclic) systems and from this point of view all results obtained find a reasonable explanation. Indeed, a comparison of k_{obs} measured in 0.1 M Na_2SO_4 at pH ~ 6 and in 0.1 M H_2SO_4 shows (see Table 1) that the effect of pH variation is observed only for Ni_2L4^{4+} and Ni_2L5^{4+}, the spin equilibria of which are most sensitive to pH, while k_{obs} for oxidation of Ni_2L2^{4+} and Ni_2L3^{4+} is practically unaffected by pH. Thus, a decrease of k_{obs} in the sequence $Ni_2L2^{4+} \sim Ni_2L3^{4+} > Ni_2L4^{4+} > Ni_2L5^{4+}$ is observed in accordance with the conclusion that the oxidation rate is determined mainly by the reactivity of the four-coordinated form of the nickel(II) complexes, *i.e.*, $k^{ls} \gg k^{hs}$.

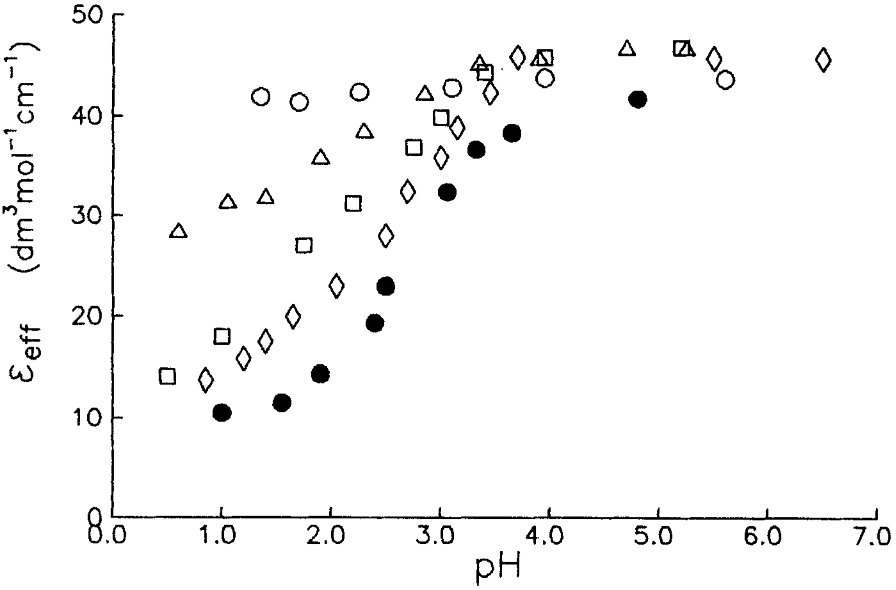

Figure 2 The dependence of ε_{eff} on pH for mono- and bis-macrocyclic nickel(II) complexes in 0.2 mol dm^{-3} (H + Na)$_2$SO$_4$, I = 0.6 mol dm^{-3}, T = 295 K: (○) - [Ni$_2$L2]$^{4+}$, (△) - [Ni$_2$L3]$^{4+}$, (□) - [Ni$_2$L4]$^{4+}$, (◊) - [Ni$_2$L5]$^{4+}$, (●) - [NiL1]$^{2+}$.

The proposed scheme also explains variations in effective activation parameters (Table 1). Oxidation of a system containing predominantly four-coordinated forms of complexes (0.1 M Na$_2$SO$_4$, pH ~ 6) is characterized by less positive activiation enthalpy and more negative activation entropy than the oxidation of complexes occurring mainly in the six-coordinated form (0.1 M H$_2$SO$_4$). Values of $\Delta H^{\neq}_{eff}$ and $\Delta S^{\neq}_{eff}$ measured in weakly acidic solution do not depend on the ligand structure and coincide within the limits of experimental error. In more acidic medium the regular increase of activation parameters is observed with the lengthening of the polymethylene chain (Figure 3). Rewriting (*8*) taking into account $k^{ls} \gg k^{hs}K_{SE}$, we obtain (*9*).

$$k_{obs} \cong k^{ls}/(1 + K_{SE}) \qquad (9)$$

At pH ~ 6, $K_{SE}<1$ for all complexes studied and $k_{obs} \cong k^{ls}$. In such case the activation parameters are related only to electron transfer in four-coordinated form (*i.e.*, $\Delta H^{\neq}_{eff} \approx \Delta H^{\neq(ls)}$ and $\Delta S^{\neq}_{eff} \approx \Delta S^{\neq(ls)}$). If equilibrium (*6*) is shifted to the right (*i.e.*, $K_{SE} > 1$, as is the case in 0.1 M H$_2$SO$_4$), (*10*) is obtained.

$$k_{obs} \cong k^{ls}/K_{SE} \qquad (10)$$

In this situation $\Delta H^{\neq}_{eff} \approx \Delta H^{\neq(ls)} - \Delta H°$ and $\Delta S^{\neq}_{eff} \approx \Delta S^{\neq(ls)} - \Delta S°$, with $\Delta H°$ and $\Delta S°$ being the thermodynamic parameters of equilibria *(6)*.

It has been demonstrated with a large number of tetraazamacrocyclic nickel(II) complexes that $\Delta H° < 0$ and $\Delta S° < 0$.[12,13] In light of this, variations of activation

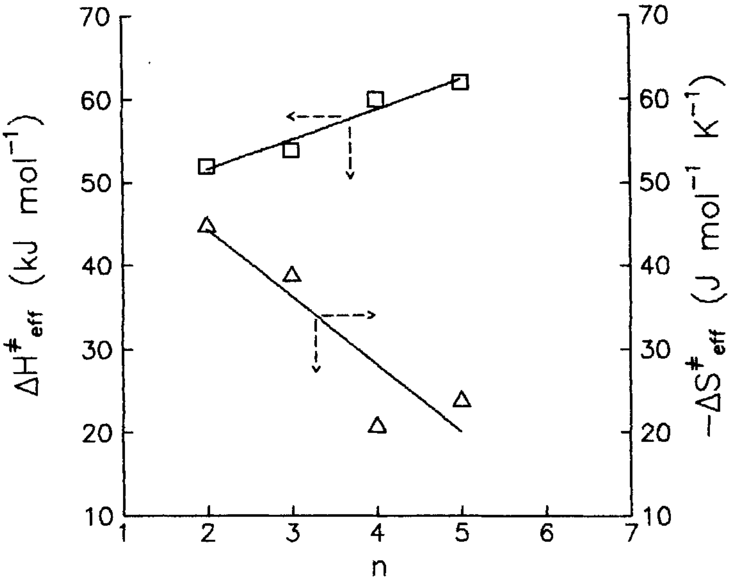

Figure 3 The dependence of $\Delta H^{\neq}_{eff}$ (□) and $\Delta S^{\neq}_{eff}$ (△) for peroxodisulfate oxidation of nickel complexes in 0.1 M H_2SO_4 on the number of methylene links (n) in connecting chain.

parameters with changing acidity and length of connecting chain are well explained. Since the activation parameters are determined from the temperature dependence of k_{obs} which are related to K_{SE} by (*9*), then

$$\Delta G^{\neq}_{eff} = \Delta G^{\neq(ls)} - f(K_{SE})\Delta G^{\circ} \qquad (11)$$

where $f(K_{SE}) \rightarrow 0$ at $K_{SE} \rightarrow 0$ and $f(K_{SE}) \rightarrow 1$ at $K_{SE} \rightarrow \infty$. In other words, increase of K_{SE} leads to an increase of the contribution of thermodynamic parameters of equilibria (*6*) in the effective activation parameters. From the data obtained one may estimate how great the intermetallic distance in the bis(macrocyclic) molecule must be for the compound to behave as a monomacrocycle. As a measure proportional to the metal-metal distance, the number of methylene groups in the connecting chain is chosen because it has been shown that such molecules adopt a conformation with maximally separated positive centres.[16] Comparison of activation parameters for $NiL1^{2+}$ oxidation with data presented in Figure 3 shows that such is the case with $n \approx 6$ to 7, although the fact that the second term in (*11*) is non-linear in the parameter n, makes such an extrapolation only approximate.

Hence, we can conclude that the kinetic parameters for peroxodisulfate oxidation of bis(macrocyclic) nickel(II) complexes are unaffected directly by the spatial structure of the reductants (*i.e.*, by the distance between metallic centres in ditopic molecules), although this may not be the case for other oxidants. More important in the systems under consideration seems to be the influence of the coordination number of nickel(II) which, all other factors being the same, is determined by the length of polymethylene chain linking the two macrocyclic subunits.

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