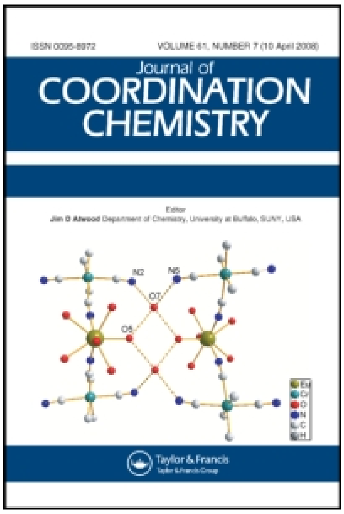

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REDOX BEHAVIOUR OF DIOXOTETRAAZA MACROCYCLIC NICKEL COMPLEXES IN AQUEOUS SOLUTION: THE APPEARANCE OF TWO METAL CENTRED REDOX PROCESSES

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$Ni^{III/II}(L)^{+/0}$ couple potentials have been measured in aqueous solutions for complexes with 14- and 13-membered macrocylic (**1** and **3**) and open-chain (**2**) dioxotetraaza ligands. The latter couple was shown to be *quasi*-reversible with $E_{1/2}$ 0.64 V *vs* SCE (0.1 M $NaClO_4$). For the macrocyclic complexes two *quasi*-reversible processes can be observed depending on the pH of the solution. Higher $E_{1/2}$ values of *ca* 0.8 and 0.9 V *vs* SCE for Ni(**1**) and Ni(**3**), respectively, are coincident with those accepted in the literature as $Ni^{III/II}(L)^{+/0}$ couple potentials. It is shown, however, that they refer actually to the redox transition in complexes with oxidized macrocyclic derivatives of **1** and **3** containing azomethine bonds formed as a result of base-catalyzed transformation of $Ni^{III}(L)^+$. The true potentials of the $Ni^{III/II}(L)^{+/0}$ couple are considerably less positive: 0.58 and 0.79 V *vs* SCE for Ni(**1**) and Ni(**3**), respectively (0.1 M $NaClO_4$). $E_{1/2}$ values for Ni(**1**)–Ni(**3**) are lower than those of complexes with polyamine analogues $Ni(\mathbf{4})^{2+}$–$Ni(\mathbf{6})^{2+}$, supporting the higher effectiveness of deprotonated amide *vs* amine donor groups in thermodynamic stabilization of nickel(III). As well as for oxo-free polyamines, the 14-membered ligand **1** provides the lowest redox potential among 12- to 15-membered dioxomacrocycles.

KEYWORDS: Nickel(II), nickel(III), dioxotetraazamacrocycles, redox potentials, electrochemistry

INTRODUCTION

Polyamine macrocycles and open-chain oligopeptides represent two most important classes of nitrogen donor ligands capable of both thermodynamic and kinetic stabilization of "non-traditional" oxidation states of transition metal ions, in particular of copper(III) and nickel(III). Such a stabilizing effect was ascribed mainly to the cyclic nature of ligands in the former[1,2] and to the strong σ-donor properties of deprotonated amide groups in the latter case.[3] It could be expected that the ligands possessing both these structural features will display enhanced stabilizing effectiveness, and the majority of the data available on macrocyclic oxopolyamine complexes agree well with such an assumption.[4]

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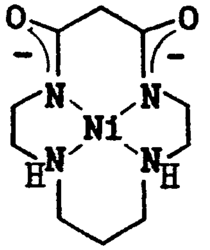
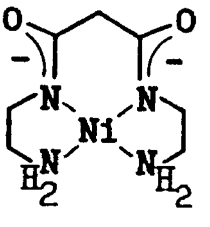
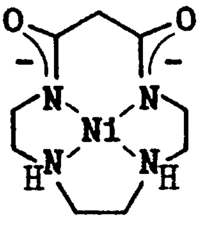


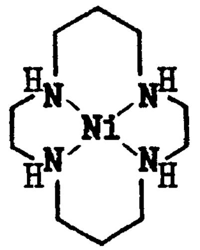
Ni(1)



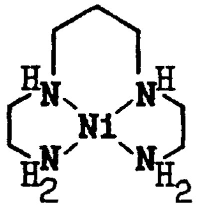
NI(2)



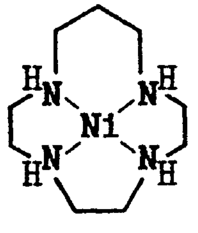
Ni(3)



$Ni(4)^{2+}$



$Ni(5)^{2+}$



$Ni(6)^{2+}$

However, in the very important case of the 14-membered ligand **1**, the dioxo derivative of cyclam (**4**), there is an uncertainty arising from the existence in the literature of two sets of $Ni^{III/II}$ $(\mathbf{1})^{+/0}$ couple potentials. In earlier works, relatively low $E_{1/2}$ values have been reported: 0.56 V in 1.0 M KCl[5] and 0.61 V in 7.0 M $NaClO_4$[6] (all potentials throughout this paper are referred to saturated calomel electrode, SCE). On the contrary, much higher redox potentials for this compound: 0.81 V in 0.5 M Na_2SO_4[4,7,8] and 0.813–0.863 V in perchlorate-containing solutions (0.1 to 7.0 M $NaClO_4$)[9] have been communicated in other papers. It is worth noting that medium effects are too small to explain the discrepancy of *ca* 0.2 V between these series of data.

Higher value of *ca* 0.8 V is now accepted in the literature as the true potential of the $Ni^{III/II}$ $(\mathbf{1})^{+/0}$ couple,[10] although this leads to obvious contradictions. First, the complex Ni(**1**) appears to have a higher redox potential as compared to $Ni(\mathbf{4})^{2+}$ (0.70–0.75 V in perchlorate- and 0.45–0.49 V in sulfate-containing media),[11,12] so that quite unexpected destabilization of nickel(III) in complex with negatively charged amide-containing ligand occurs. Secondly, this means that the nickel(III) complexes with the 12- and 15-membered dioxotetraaza macrocycles ($E_{1/2}$ = 0.62 V in 0.5 M Na_2SO_4 in both cases)[4,7,13] are much more stable thermodynamically than the complex with the 14-membered ligand, while for polyamine analogues $Ni(\mathbf{4})^{2+}$ has the lowest redox potential.[2]

Unfortunately, no reasonable explanation of these facts exists in the literature. On the other hand, we have found recently that $Ni^{III/II}(L)^{+/0}$ redox potentials of complexes with open-chain dioxotetraaza ligands, in particular of Ni(**2**), are in all cases far below 0.8 V.[14] Moreover, our preliminary data indicated that the $E_{1/2}$ value of Ni(**1**) is more likely to equal 0.6 rather than 0.8 V.[15] All these contradictions stimulated us to carry out a reinvestigation of redox properties of Ni(**1**) as well as of the complex with the 13-membered homologue, **3**.

EXPERIMENTAL

Reagents

All reagents used were of reagent grade. Ligands H_2**1**, H_2**2** and H_2**3** and their nickel(II) complexes were obtained as previously described.[16–18]

Instrumentation and electrochemical measurements

Electronic absorption spectra were recorded on a Specord UV-VIS (Karl Zeiss, Jena) spectrophotometer; pH was controlled using a EV-74 (Izmeritel, Gomel) pH meter.

Cyclic voltammograms were generated using a PI-50-1.1 potentiostat equipped with a PR-8 function generator (both Izmeritel, Gomel) and an N-307 X-Y recorder (ZIP, Krasnodar). A standard three electrode system consisting of glassy carbon working, saturated calomel reference and Pt wire auxiliary electrodes was used. The following procedure of pre-conditioning of the working electrode was used before each measurement. The electrode was cycled at a sweep rate of 500 mV/s for about 10 minutes in 0.1 M $NaClO_4$ solution between potential limits of *ca* −2 and +2 V followed by several dummy scans on an electrolyte in the potential region of interest.

RESULTS AND DISCUSSION

Electrochemical behaviour of the nickel complexes with dioxotetraamines is rather sensitive to the electrode material. Our, as well as other authors',[13] attempts to obtain reversible CV responses on a platinum working electrode were unsuccessful. Better results were obtained on a glassy carbon electrode, but satisfactory reversibility was achieved only after the special pre-treatment of the electrode surface (see Experimental), analogous to that used by Margerum *et al.*[3] in the study of the redox properties of peptide complexes.

Our results concerning complex with the noncyclic ligand Ni(**2**) provide a good illustration of this fact. We were able to obtain cyclic voltammograms of this compound with good reversibility (see Fig. 1) in drastic contrast to the literature, where the $Ni^{III/II}$(**2**)$^{+/0}$ couple is reported to be irreversible.[4,7]

Cyclic voltammograms of the nickel complex with the 14-membered ligand **1** have been measured in the presence of different electrolytes and in all cases they can be treated as *quasi*-reversible with cathodic-to-anodic peak current ratios, i_{pc}/i_{pa}, close to 1 and peak-to-peak separation, ΔE, ranging from 70 to 90 mV (Table I, Fig. 1).

Rather good reversibility (especially at high concentrations of supporting electrolyte) typical of oxidation/reduction of the metal centre may be considered as evidence that we really deal with the nickel(II)/nickel(III) transition. In agreement with the low net charge (+1) of the nickel(III) complex with a dianionic ligand, the

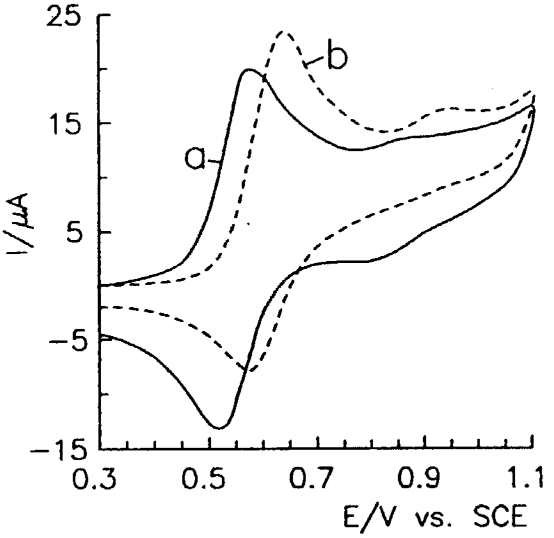


Figure 1 Cyclic voltammograms of complexes Ni(**1**) (*a*) and Ni(**2**) (*b*) (0.5 M Na_2SO_4; [NiL] = 3.0×10^{-3} M; 50 mV/s; pH 7.5 and 8.0, respectively).

value of $E_{1/2}$ does not depend strongly on the nature and concentration of electrolyte (Table I). In particular, the decrease of redox potential in the presence of coordinating anions (Cl^-, SO_4^{2-}) is less than 50 mV.

In all cases $E_{1/2}$ values obtained do not exceed 0.6 V (Table I) and are practically coincident with those obtained earlier.[5,6] Nevertheless, close inspection of cyclic voltammograms (Fig. 1) reveals, along with the main peaks in low-potential region, the presence of additional peaks at higher potentials.

Since the sole obvious difference in conditions used previously[4,7] and in the present work is the pH of solution (9 and 7.5, respectively)[19] we have carried out the electrochemical study of Ni(**1**) at different pH values. As follows from data obtained, cyclic voltammograms of this compound remain almost unchanged up to a pH of *ca* 9.5. Further increase of pH leads to the appearance of a number of additional anodic peaks in the low-potential region which are probably caused by adsorption, and to the growth of peaks centred at *ca* 0.8 V. The high-potential redox process becomes quite distinct at pH 11 (Fig. 2) and its $E_{1/2}$ value of 0.81 V is in

Table I $Ni^{III/II}(L)^{+/0}$ redox potentials in aqueous solution[a].

Complex	Electrolyte	$E_{1/2}$/V *vs* SCE	ΔE/mV
Ni(**1**)	0.1 M $NaClO_4$	0.58	90
	3.0 M $NaClO_4$	0.60	70
	1.0 M KCl	0.55	70
	0.5 M Na_2SO_4	0.55	70
Ni(**2**)	0.1 M $NaClO_4$	0.64	90
	0.5 M Na_2SO_4	0.61	65
Ni(**3**)	0.1 M $NaClO_4$	*ca* 0.79[b]	*ca* 150
	0.5 M Na_2SO_4	*ca* 0.75[b]	*ca* 100

[a] At 20°C, glassy carbon electrode, scan rate 50 mV/s. [b] Scan rate 500 mV/s.

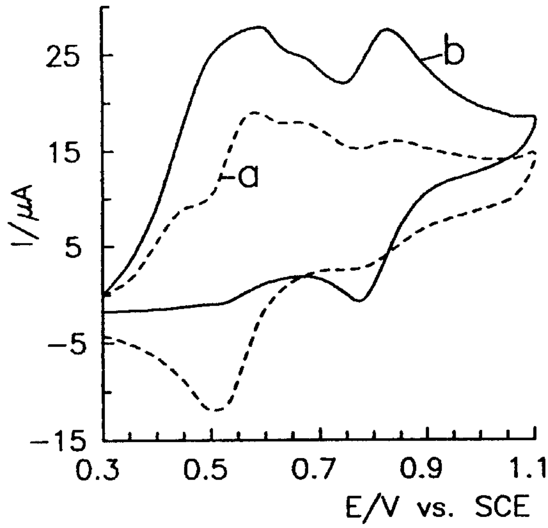
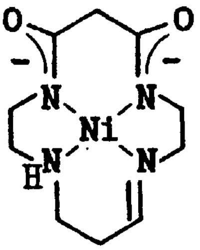


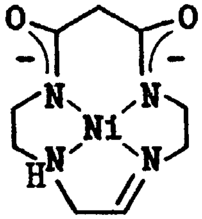
Figure 2 Cyclic voltammograms of Ni(1) at pH 10.3 (*a*) and pH 11.0 (*b*) (0.5 M Na_2SO_4; [NiL] = 3.0×10^{-3} M; 50 mV/s).

excellent agreement with that accepted in literature[4,7-10] as the true $Ni^{III/II}(\mathbf{1})^{+/0}$ couple potential. Thus, both processes with $E_{1/2}$ values of 0.55 and 0.81 V can be observed for this complex, depending on conditions.[20] As follows from the arguments presented earlier,[9,18] the second redox reaction is also a metal-centred process.

Let us consider the reasons which could lead to the appearance of such a phenomenon in the systems under consideration. It is well known that nickel(III) macrocyclic amine complexes are kinetically unstable in alkaline media and transform *via* a base-catalyzed pathway to nickel(II) compounds with oxidized ligands containing azomethine bonds.[21] We have shown recently[22] that an analogous process occurs in case of $Ni^{III}(\mathbf{1})^+$ and $Ni^{III}(\mathbf{3})^+$ leading to complexes Ni(**7**) and Ni(**8**), respectively. The presence of the azomethine bond in these structures was confirmed by ^{13}C and ^{1}H NMR and electronic absorption spectra.[22]



Ni(7)



Ni(8)

The metal centre in Ni(7) can be oxidized further, giving a second metal-centred process, so that the electrochemical behaviour of Ni(**1**) in alkaline solutions should be treated in terms of an ECE mechanism. It is worth to note that the appearance of C=N bonds in the ligand should increase the redox potential of the complex.[1]

To obtain direct evidence for such an assumption, we have studied electrochemical properties of the nickel(II) complex Ni(7) generated *in situ* using both electrochemical oxidation at a Pt anode at constant potential of 0.6 V and chemical oxidation by peroxodisulfate. The content of Ni(7) in the reaction mixture was followed by its characteristic UV band (Fig. 3A). The intensity of this band is proportional to the charge consumed in the course of the electrolysis yielding an ε value of 2650 ± 150 $M^{-1}cm^{-1}$ for the complex containing a single C=N bond (two moles of electrons consumed per mole of starting compound), in rather good agreement with our previous estimate.[22] It is obvious from Figure 3 that the effectiveness of the process with $E_{1/2}$ of 0.8 V correlates well with the content of Ni(7) in solution. Thus, the above data show unambiguously that the redox potential of *ca* 0.8 V actually refers not to the complex Ni(**1**) but to its oxidized derivative Ni(7).

The reversible pattern for the process at 0.8 V can be observed at pH values as high as 11 (Fig. 2), while for the starting complex cathodic peak corresponding to reduction of the nickel(III) disappears completely under such conditions. This implies much higher kinetic stability (in the time scale of cyclic voltammetry) of $Ni^{III}(7)^+$ as compared to $Ni^{III}(\mathbf{1})^+$ in spite of the higher redox potential of the former. In our opinion, this fact may be explained by taking into account the fact that the number of possible pathways for transformation of nickel(III) complex will diminish with the decrease of the number of available NH-groups.[21] The relatively high kinetic stability of the nickel(III) complex $Ni^{III}(7)^+$ along with the difficulties in obtaining good electrochemical reversibility seem us to be the main reasons for the appearance of the problem discussed in this paper.

Analogous investigations, have been carried out for the nickel complex with the 13-membered macrocycle **3** whose redox potential was reported to be *ca* 0.9 V.[4,7–9] The CV responce of Ni(**3**) (Fig. 4) in neutral solution resembles that of the 14-membered analogue, but at much higher pH, in two respects: the complete absence of any cathodic peak corresponding to the first anodic peak (at a sweep rate of 50 mV/s) and the presence of the reversible pattern in the high-potential region with $E_{1/2}$ of 0.9 V, *i.e.* coincident with the accepted value of the redox potential for the $Ni^{III/II}(\mathbf{3})^{+/0}$ couple. The effect of the increase of pH on the shape of CV curves is not so pronounced in this case. Increase of the potential sweep rate to 500 mV/s results in the appearance of a cathodic peak in the low-potential region and suppression of the process at 0.9 V, as should be expected for an ECE mechanism. This behaviour is consistent with much lower kinetic stability (*ca* four orders of magnitude)[22] of $Ni^{III}(\mathbf{3})^+$ as compared to $Ni^{III}(\mathbf{1})^+$.

For the reasons outlined above, we believe that an $E_{1/2}$ value of 0.9 V must be assigned to the metal centred redox process in the complex of oxidized ligand Ni(**8**), with the true $Ni^{III/II}(\mathbf{3})^{+/0}$ redox potential being considerably lower. Unfortunately, the presence of an additional pre-peak on the cyclic voltammograms prevents precise determination of $E_{1/2}$ but it can be estimated to be *ca* 0.8 V. Although the redox potential of this complex is rather high it is still lower than that of the polyamine analogue $Ni(\mathbf{6})^{2+}$ (0.9 V in 0.5 M $NaClO_4$).[23]

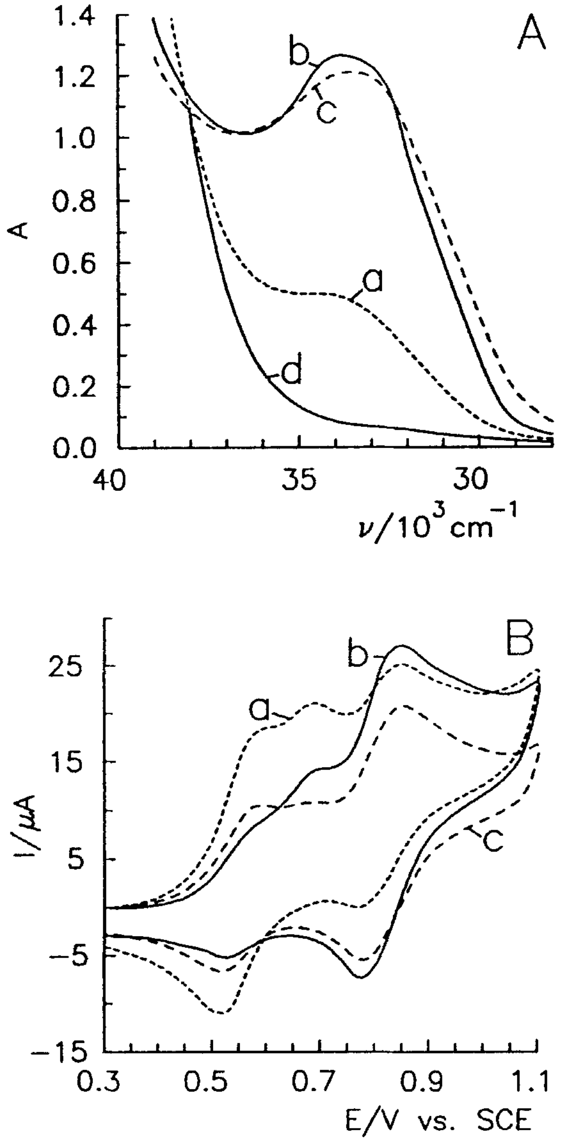


Figure 3 Electronic absorption spectra of oxidized solutions of Ni(**1**) (A) and corresponding cyclic voltammograms (B): (*a*), (*b*) consecutive stages of electrochemical oxidation: 0.6 and 1.9 moles of electrons consumed per mole of starting complex, respectively; (*c*) oxidation by equimolar amounts of $K_2S_2O_8$; (*d*) spectrum of the starting complex (0.5 M Na_2SO_4; pH 7.5; [NiL] = 2.5×10^{-3} M; 50 mV/s; optical path length 0.2 cm).

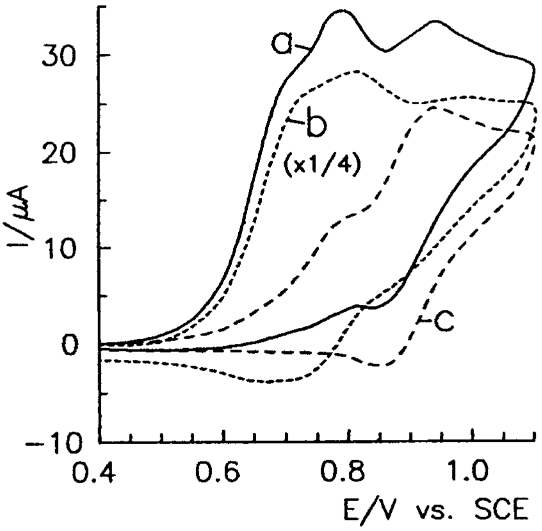


Figure 4 Cyclic voltammograms of Ni(3): (*a*) 50 mV/s; (*b*) 500 mV/s; (*c*) solution oxidized by equimolar amounts of $K_2S_2O_8$, 50 mV/s (0.5 M Na_2SO_4; pH 7.5; [NiL] = 5.0×10^{-3} M).

Thus, our results on the electrochemical properties of nickel complexes with **1** and **3** support the conclusion that redox potentials of complexes with dioxotetraaza ligands are always lower than those of complexes with polyamine analogues in the absence of coordinating anions like SO_4^{2-}, Cl^- *etc.*, *i.e.*, the replacement of amine donor groups by deprotonated amides leads to the thermodynamic stabilization of nickel(III) with no exception. However, such a replacement results also in the decrease of the net positive charge of complex species thus leading to the considerable weakening of axial interactions in nickel(III) compounds and the reverse pattern is often observed in media containing high concentrations of coordinating anions.

The data obtained show that the 14-membered macrocycle **1** is the most effective ligand in stabilization of nickel(III) among all 12–15-membered dioxotetraaza macrocycles studied. In addition, it is noted that the stabilizing effect of this ligand as compared to its open-chain analogue **2** (60 mV) is very close to that observed in the related oxofree pair (80 mV for $Ni(\mathbf{4})^{2+}$ *vs* $Ni(\mathbf{5})^{2+}$),[12] clearly indicating the similarity of structural factors for these two types of compounds in the lowering of the $Ni^{III/II}(L)^{+/0}$ redox potential.

Acknowledgements

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