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A new ditopic receptor containing tetraazamacrocyclic and crown ether fragments. Synthesis, spectral characteristics, and redox behavior

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A new ditopic molecule consisting of nickel azamacrocyclic and crown ether subunits has been synthesized via Schiff base condensation between formylbenzo-15-crown-5 and the pendant amino group of nickel(II) tetraazamacrocyclic complex. The structure of this compound has been confirmed by elemental analysis, IR, electronic absorption spectrocopy, and FAB mass spectrometry. A substantial cathodic shift of the Ni(III)/Ni(II) redox potential was observed for this ditopic molecule in the presence of ammonium salts. This is in contrast to the ammonium ion induced anodic shifts observed for other ditopic molecules containing crown ether and redox active fragments. The interactions of parent monomacrocyclic and ditopic nickel(III) complexes with some bifunctional reductants were investigated. The electrochemical and kinetic results were explained in terms of an "open"—"closed" conformational equilibrium for the bis-macrocyclic molecule and supramolecular complex formation through two-centered substrate—receptor interaction.

INTRODUCTION

Current progress in macrocyclic chemistry gives one the possibility to synthesize a wide variety of different compounds. The application of molecular design principles allows one to create, on the basis of these compounds, a new generation of reagents and catalysts similar to enzymes. From our point of view, ditopic molecular systems containing both redox and receptor centers are of interest as enzyme models. It is convenient to use extremely thermodynamically stable transition metal complexes with azamacrocycles[1] as redox centers. The well-known capability of azamacrocyclic ligands to stabilize unusual oxidation states of coordinated ions[2] can facilitate reversible electron transfer processes involving the metal ion and substrate molecules. Host-guest interactions provide an appropriate way for the receptor center to bind and orient the substrate. This type of interaction can be realized by means of complexation of alkylammonium ions to crown ethers[3]. Therefore bis-macrocyclic compounds containing azamacrocyclic transition metal complexes and crown ether subunits should possess both redox and molecular recognition properties during reactions with bifunctional substrates.

Several examples of ditopic macrocyclic molecules containing transition metal and ammonium ion binding sites are known. Among them are transition metal porphyrins[4], phthalocyanines[5] and oximes[6] bearing crown ether substituents; monomacrocyclic compounds with nitrogen and oxygen donor atoms (1[7] and 2[8]); and the bis-macrocycle 3[9]. The results obtained show that these compounds are capable of forming heterobimetallic complexes with transition and alkaline metal ions. Moreover, complexes of 2 with UO_2^{2+} and urea were isolated and characterized.[8] Kimura and coworkers have shown that 3 is an efficient receptor for ionic organic substrates such as aminoacids, peptides and catecholamines[9]. Furthermore, it was determined that the supramolecular complexes are formed by a two-centered interaction: the ammonium group of the substrate is bound by the crown ether, while the acidic group of the substrate interacts with the protonated azamacrocycle.[9] All of the works cited, however, are concerned only with the static properties of supramolecular compounds formed in the solid state and in solutions. The chemical

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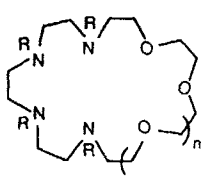
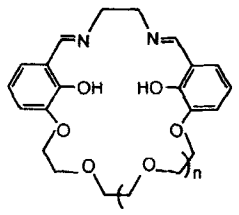
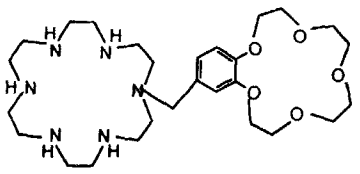


1 R = -H, $-CH_2COOH$

n = 1, 2, 3, 4



2 n = 1, 2, 3, 4, 5



3

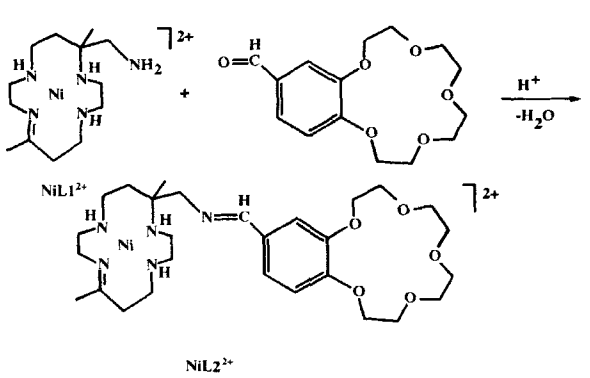
reactivity of these supramolecular compounds is not addressed.

The goals of the work presented here were the synthesis of a new ditopic compound consisting of receptor (crown ether) and redox active (tetraazamacrocyclic nickel complex) fragments; the study of its spectral and electrochemical characteristics; and the understanding of its peculiar redox interactions with bifunctional organic substrates, as compared to the behavior of the parent monomacrocyclic nickel complex without a crown ether unit.

RESULTS AND DISCUSSION

Synthesis and spectral characteristics of the ditopic compound

The ditopic complex was prepared by azomethine bond formation between formylbenzo-15-crown-5 and the pendant amino group of the macrocyclic nickel complex, $[NiL1](ClO_4)_2$.



NiL1^{2+}

NiL2^{2+}

Many such aromatic Schiff bases are known to form readily under mild conditions[10]. The reaction outlined above, however, requires the presence of an acid catalyst. The equilibrium is shifted to the right by distilling off the condensation byproduct (water) in an azeotropic mixture with ethanol and benzene. The necessity for these relatively strong reaction conditions may be the consequence of deactivation of the primary amino group in $[NiL1]^{2+}$ by the neighbouring positively charged nickel(II) ion. An analogous effect was observed earlier in attempts to prepare a Schiff base compound from the apical amino groups of $[Co(diAMsar)]^{3+}$ (diAMsar = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6] eicosane).[11] In addition to its well-known role as a catalyst in Schiff-base condensations, the acid catalyst in the present reaction may also protonate the pendant amino group. Protonation of the pendant amine frees it from the nickel ion thus making it available for condensation with the carbonyl group of the crown ether. It should be noted, additionally, that the use of the macrocyclic complex, instead of the free ligand, in the condensation reaction prevents side reactions involving secondary amines. The coordinated metal ion therefore plays the role of a protecting group.

FAB mass spectroscopy has proven useful in establishing the ditopic formulation of the new compound. The mass spectrum of $[NiL2](ClO_4)_2$ shows three groups of peaks at m/z 690, 591, and 280 (only the main peak in each group is quoted) which correspond to $[NiL2 + ClO_4]^+$, $[NiL2]^+$, and the benzocrown ether moiety resulting from azomethine bond cleavage, respectively. The peak with m/z 690 is the base peak in the mass spectrum. The perchlorate ion in this species may be involved in hydrogen bonding to the N-H groups, an interaction that might facilitate its vaporization as a part of the complex cation.

The IR spectrum of $[NiL2](ClO_4)_2$ also confirms its bismacrocyclic structure. It contains all of the absorbances of the starting reagents except the $[NiL1]^{2+}$ pendant amino group stretching absorbances at 3250 and 3160 cm^{-1} and the formyl-B15C5 carbonyl stretch at 1700 cm^{-1}. In addition, a strong band at 1640 cm^{-1}, assigned to C = N stretching mode, appears in the spectrum of $[NiL2]^{2+}$.

The electronic absorption spectra of $[NiL2]^{2+}$, in aqueous and acetonitrile solutions, contain a number of strong bands in the UV region associated with the presence of a benzene ring in the crown ether fragment [43 500 cm^{-1} (ε = 11 600 M^{-1} cm^{-1}), 35 200 cm^{-1} (7500), and 32 000 cm^{-1} (6 400)]. Only one weak band is present in the visible region of the spectrum [H_2O: 21 800 cm^{-1} (ε=30); CH_3CN: 22000 cm^{-1} (ε=40)]. The energy of this band is characteristic of low-spin square-planar

nickel(II) complexes with 14-membered tetraazamacrocycles, while its intensity is much lower (typical values of ε for such compounds lie in the range 60 – 90 M^{-1} cm^{-1}).[1] It is evident from the spectral data that the ditopic complex exists, in aqueous and acetonitrile solutions, as an equilibrated mixture of hexacoordinated high-spin and square-planar low-spin forms. This conclusion follows from the knowledge that the high-spin form is characterized by visible absorption bands with very low extinction coefficients (ε < 10 M^{-1} cm^{-1}) [1,12]. To a first approximation the presence of the high-spin form in solution can be detected by the low extinction coefficient of the band at *ca.* 22 000 cm^{-1} relative to the corresponding extinction coefficients for typical low-spin complexes.

Spectral characteristics of $[NiL1]^{2+}$ [H_2O: 20 000 cm^{-1} (ε = 15 M^{-1} cm^{-1}); CH_3CN: 20 400 cm^{-1} (ε = 15)] also indicate the presence of a significant amount of the hexacoordinated form which decreases sharply after acidification of the solutions [22 500 cm^{-1} (ε = 84) and 22 000 cm^{-1} (ε = 65) in water and acetonitrile containing 0.01 M $HClO_4$, respectively]. This process is caused by the protonation of the pendant amino group leading to its decoordination. In contrast, the intensity of the d-d band of $[NiL2]^{2+}$ does not depend on the pH of the solutions. This confirms the absence, in the ditopic molecule, of a donor amino group which would be able to interact either with the metal ion or with the proton.

Redox properties of the nickel compounds

Cyclic voltammograms of $[NiL2]^{2+}$ measured in aqueous 0.1 M $NaClO_4$ and of $[NiL1]^{2+}$ in an acidic aqueous medium show a quasireversible (ΔE = 100 mV, i_{pc}/i_{pa} ca. 1) wave with $E^{1/2}$ = 0.65 V which corresponds to nickel (II)/(III) oxidation. This assignment is based on the spectral characteristics of the products formed (see below) and the data described earlier[14]. In addition, a poorly resolved peak at ca. 0.9 V is observed in the anodic part of the voltammogram of $[NiL2]^{2+}$ in aqueous solution.

Keeping in mind that more effective interactions between the receptor fragment of the ditopic molecule (crown ether) and the substrate (e.g., ammonium group) are expected in non-aqueous solutions than in water[3], we have performed more detailed studies on the redox properties of the nickel complexes in acetonitrile. The choice of this solvent is justified by its ability to dissolve the species of interest, its ability to stabilize the nickel(III) compounds[13], and its redox stability at the potentials applied.

The main feature of both complexes in acetonitrile is the presence of two quasi-reversible oxidation processes (Table 1 and Fig. 1). The potentials of the first wave ($E_{1/2}^1$ ca. 1 V) are typical of Ni(III)L/Ni(II)L couples in similar macrocyclic environments[13]. The second process ($E_{1/2}^2$ ca. 1.3 V) should not be assigned to ligand oxidation because of its relatively low potential and quasi-reversibility. These features also allow us to discard from consideration the oxidation of nickel(III) to nickel(IV). Such processes become possible only at potentials higher than 1.7 V (see, for example,[14]).

Existing data concerning the electrochemical behavior of macrocyclic nickel complexes with pendant amino groups [e.g. N-aminoethylcyclam[15] and 5-aminomethyl-5,12-dimethylcyclam[16] (cyclam = 1,4,8,11-tetraazacyclotetradecane)], in aqueous solution, indicate that protonation of the pendant amino group causes the appearance

Table 1 Redox potentials (V vs. SCE) of $[NiL]^{3+/2+}$ couples in acetonitrile[a]

L	*Additives*	$E_{1/2}^1$	$E_{1/2}^2$
L1	—	0.98 (80)	—
	0.01 M $HClO_4$	0.99 (100)	1.21 (110)
	0.01 M $HClO_4$ + 0.2 M $[MeNH_3]ClO_4$	0.99 (95)	1.21 (110)
	0.01 M $HClO_4$ + 0.2 M [β-AlaH]ClO_4	0.95 (80)	1.18 (100)
L2	—	1.01 (105)	1.27 (110)
	0.01 M $HClO_4$	0.95 (60)	1.25 (60)
	0.01 M $HClO_4$ + 0.2 M $[MeNH_3]ClO_4$	0.85 (130)	1.18 (120)
	0.01 M $HClO_4$ + 0.2 M [β-AlaH]ClO_4	0.79 (110)	1.14 (90)

[a] 0.1 M $[(n\text{-}Bu)_4N]BF_4$, 25°C, sweep rate 100 mV/s, peak-to-peak separations (mV) are given in parentheses.

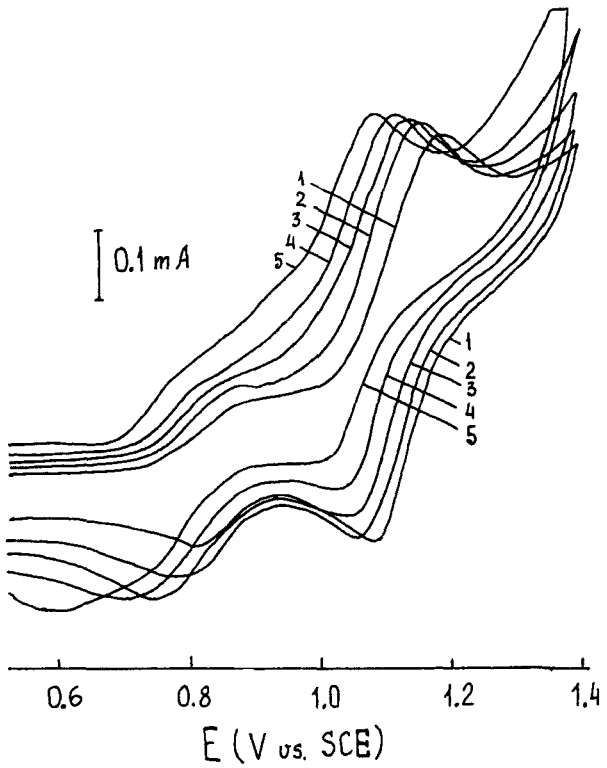


Figure 1 Cyclic voltammograms of $[NiL2]^{2+}$ in the presence of β-alanine hydroperchlorate (acetonitrile solutions containing 0.01 M $HClO_4$ and 0.1 M $[(n\text{-}Bu)_4N]BF_4$). Concentrations of substrate: none (1), 3×10^{-2} M (2), 5×10^{-2} M (3), 1×10^{-1} M (4), and 2×10^{-1} M (5).

of an additional high potential redox peak in the CV. These results are explained by two factors. 1) The pendant amino group, which is initially bound to the metal, is replaced by a water molecule upon protonation. The water molecule does not stabilize the Ni(III) oxidation state as well as the amine. 2) The presence of a positively charged ammonium group in the immediate vicinity of a highly charged Ni(III) ion is destabilizing. The same factors explain the CV characteristics of $[NiL1]^{2+}$. They are in a good agreement with spectral data which show a predominance of the high-spin form of $[NiL1]^{2+}$ in pure acetonitrile with a detectable increase in the content of low-spin complex after acidification. Moreover, the difference between $E_{1/2}^1$ and $E_{1/2}^2$ in our case (220 mV) is very close to the value obtained for a structurally similar nickel complex with reduced L1 ligand (210 mV).[16]

Because of structural reasons, analogous arguments do not suitably explain the electrochemical properties of ditopic complex $[NiL2]^{2+}$. We contend that the azomethine group is unable to bind the nickel ion because of its bulky crown ether substituent. The pH independence of the absorption spectra of $[NiL2]^{2+}$ supports this contention.

Another way of looking at the appearance of two peaks the in CV of $[NiL2]^{2+}$ is to consider the possibility of axial crowding in the ditopic molecule. It was shown earlier that the presence of substituents on the macrocyclic backbone (for example, an axially oriented methyl group on a 6-membered chelate ring) causes a shift of the Ni(III)L/Ni(II)L couple potential to more positive values[17]. Since nickel(III) complexes with noncharged tetraamine ligands are uniquely six-coordinated irrespective whether the starting nickel(II) compounds have coordination number 4 or 6[13], this shift in potential is due to the energy consumed in changing the macrocyclic conformation to minimize the steric repulsion between substituents and axially coordinated solvent molecules. It is obvious from this point of view that hexacoordinate nickel(II) complexes will be oxidized at less positive potentials than square-planar species are, because less inner coordination sphere reorganization energy is needed during the oxidation.

Normally, however, the occurence of nickel(II) amine complexes as a mixture of high- and low-spin forms in solution does not result in the appearance of two peaks in the CV (see, for example,[18]). The reason for this may be the high rate of axial ligand exchange inherent to nickel(II) and nickel(III) macrocyclic complexes[19]. For $[NiL2]^{2+}$ one can expect that the presence of a bulky substituent on the tetraazamacrocycle will reduce the conformational flexibility of the ditopic molecule and create steric hindrance for axial ligation. These effects will slow the axial ligand exchange rate causing nickel(II) complexes with accessible positions to behave differently from nickel(II) complexes with crowded axial positions on the CV time scale. Therefore, the most reasonable assumption is to assign both redox processes observed in the CV of $[NiL2]^{2+}$ to nickel(II)/(III) oxidation. The first peak is due to the oxidation of hexacoordinated nickel(II) or to the oxidation of non-hindered square-planar nickel(II) complexes. The second peak is due to the oxidation of sterically hindered square-planar compounds.

CPK models show that NiL2 can exist in solution as two limiting conformers which may be visualized in general as follows (intermediate cases must not be ruled out):

"open" "closed"

These forms are interconvertible due to the presence of a methylene group in the joining chain. It was, unfortunately, impossible to study the real conformations of $[NiL2]^{2+}$ in solution by means of NMR spectroscopy because of the presence of paramagnetic particles. Other experimental data obtained (see below) can be reasonably interpreted in light of an "open"—"closed" conformational equilibrium hypothesis. Molecular modelling (MM2, CAChe program) shows that E-Z-isomerism at the C=N double bond need not be involved in the interconvertion of "open" and "closed" conformers in the ditopic molecule. The E isomer is favorable for the "open" conformation, whereas the energies of E and Z isomers are comparable for the "closed" conformations.

Although the electrochemical data discussed above demonstrate that $[NiL1]^{2+}$ and $[NiL2]^{2+}$ have similar redox properties, the two complexes behave differently in the presence of potential substrates. As follows from Table 1, the addition of acid to an acetonitrile solution of $[NiL1]^{2+}$ has little effect on the $E_{1/2}^1$ value. This is in contrast to $[NiL2]^{2+}$ for which cathodic shifts and increased reversibility are observed for both waves. The reasons for such differences are not presently clear, but may be connected, at least in part, to interaction of hydroxonium cation with the crown ether fragment of the ditopic molecule. The consequences of such an interaction are discussed below.

Perchlorate salts of methylamine ($MeNH_3^+$) and β-alanine (β-AlaH$^+$) were chosen as substrate molecules capable of host-guest interaction with the crown ether receptor unit of the ditopic molecule. The former salt can interact only with the crown ether fragment, while the latter can, in principle, form an additional coordination bond between the carboxylic acid group and the metal(II) or (III) ion resulting in two-centered fixation of the substrate. Spectral investigation have shown, howev-

er, that the COOH-group of β-alanine does not coordinate to nickel(II) in the presence of up to an 80-fold excess of substrate. Carboxylic group coordination can therefore be expected only for nickel(III) complexes.

The electrochemical behavior of $[NiL1]^{2+}$ is not influenced by the addition of methylammonium perchlorate. Protonated β-alanine causes a slight (ca. 30 mV) cathodic shift of both $E_{1/2}$ values, an effect which is typical for the stabilization of Ni(III) by carboxylate coordination[20].

In contrast to the results for $[NiL1]^{2+}$, $[NiL2]^{2+}$ demonstrates cathodic shifts of both $E_{1/2}{}^1$ and $E_{1/2}{}^2$ in the presence of $MeNH_3^+$ (20 – 100 mV depending on the substrate concentration). A more substantial shift (up to 160 mV) is observed with β-AlaH$^+$ as an additive (Fig. 1 and Table 1). It should be noted that the presence of large excesses of substrate causes irreversibility of both redox processes for $MeNH_3^+$ but only partial loss of first wave reversibility for β-AlaH$^+$.

It was found elsewhere that the interaction of ammonium or alkali metal ions with crown ether bearing redox active substituents (e.g., ferrocenyl) results in a marked *anodic* shifts (up to 250 mV) of their redox potentials due to electrostatic destabilization of the higher oxidation state.[21] To understand the *cathodic* shifts of the $[NiL2]^{3+/2+}$ couple potentials, in the presence of ammonium salts, we must once again consider the "open"–"closed" conformational equlibrium of the ditopic molecule. We contend that crown ether–ammonium (or hydroxonium) interactions transform the molecules with "closed" conformations into predominantly "open" forms, thus maximizing the space between two positively charged centers. Analogous "open" conformations were found recently for bis-macrocyclic dimetallic complexes.[22] It is evident from general considerations that axial positions in the coordination sphere of a metal ion are more accessible in the "open" conformation. The "open" conformation facilitates the coordination of acetonitrile to nickel(III) thus shifting the redox potential to less positive values.

The difference between the two types of ditopic molecules containing crown ether and redox active centers are, therefore, a consequence of the properties of the oxidized forms of the redox fragments. For nickel complexes axial coordination of solvent molecules is very important and the stabilization of "open" oxidized forms is observed after ammonium is bound by the crown ether. In the cases of ferrocenyl, tricyanovinyl- and other substituents, the binding of cations by the crown ether causes only electrostatic destabilization of the oxidized form of the redox center.[21] It is noteworthy, that for the $[NiL2]^{3+/2+}$ couple the former effect more than compensates for the latter.

As follows from data presented in Table 1, more negative shifts of $E_{1/2}$ are observed in the presence of β-AlaH$^+$ than in the presence of $MeNH_3^+$ at the same concentrations of substrate. Apparently, two-centered coordination of protonated β-alanine to $[NiL2]^{3+}$ (but not to $[NiL1]^{3+}$) is quite resonable.

The nickel(III) complexes can be readily prepared in solution by means of electrochemical or chemical oxidation. The preparative electrolysis of acidic aqueous or acetonitrile solutions of $[NiL1]^{2+}$ and $[NiL2]^{2+}$ at 1.1 V results in quantitative formation of the appropriate nickel(III) complexes. For chemical oxidation, $Ce(SO_4)_2$ (acidic aqueous solutions) and $(NH_4)_2Ce(NO_3)_6$ or $NOClO_4$ (acetonitrile) were suitable oxidizing agents. Since the latter two oxidants do not react with the nickel(II) complexes rapidly and quantitatively, the solutions of nickel(III) complexes generated electrochemically were used for further kinetic investigations.

Both $[NiL1]^{3+}$ and $[NiL2]^{3+}$ containing solutions are adequately stable and do not decompose via intramolecular redox reactions over a period of several hours. Their authenticity is supported by absorption spectra and ESR data. The visible spectra of the nickel(III) complexes exhibit intense bands (ε=11 000 $M^{-1}cm^{-1}$) at 29 600 ($[NiL1]^{3+}$) and 29 000 cm^{-1} ($[NiL2]^{3+}$) which are typical of azamacrocyclic nickel(III) complexes.[13,14] The ESR spectra of frozen acetonitrile solutions (0.01 M $HClO_4$) are identical for both complexes ($g_{||}$ = 2.02; $g_{\perp}$ = 2.15) and characteristic of the low-spin d^7 electronic configuration in a tetragonally distorted environment (unpaired electron is localized on the d_{z2} orbital).[13]

Kinetics of redox reactions of nickel(III) complexes with organic bifunctional substrates

As was mentioned above, the redox potentials of $[NiL2]^{3+/2+}$ (but not $[NiL1]^{3+/2+}$) are influenced by host-guest complex formation between the crown ether subunit of the ditopic molecule and the ammonium group of an organic substrate. Two-centered binding by $[NiL2]^{3+}$ is suggested for β-AlaH$^+$ as a substrate. One can expect that such an interaction might also influence the redox kinetics of ditopic complexes, especially when spacial complementarity between substrate and receptor is present. To be involved in these processes a substrate molecule should contain an anchoring group to react with the crown ether and a redox active (reducing) fragment capable of interacting with nickel(III). For these reasons the reactions of 3-amino-propanol-1, m-aminophenol (AP), and β-alanine hydrazide (AH) with the nickel(III) complexes have been investigated. Since all measurements have been made in acetonitrile containing 0.01 M $HClO_4$, the protonated amino groups of these substances can behave as anchoring groups while the alcoholic, phenolic, or hydrazoic functions can be regarded as potentially reducing fragments.

It was established that 3-aminopropanol-1 reacts neither with $[NiL1]^{3+}$ nor with $[NiL2]^{3+}$. This demonstrates that the substrate–receptor interaction, if present in this

case, does not change the reactivity of macrocyclic compounds studied. The addition of either m-aminophenol or β-alanine hydrazide to solutions of either nickel(III) complex resulted in the complex being reduced to its nickel(II) form. These reduction reactions were found to be second-order

$$V = -d[NiL^{3+}]/dt = k_{obs}[NiL^{3+}][St]$$

The values of k_{obs} along with corresponding activation energies are summarized in Table 2.

The data obtained show considerable differences in the reactivity of $[NiL1]^{3+}$ and $[NiL2]^{3+}$. These differences must be explained by the simultaneous presence of reactive and receptor centers in $[NiL2]^{3+}$, because the addition of equimolar quantities of benzo-15-crown-5 to the solution of $[NiL1]^{3+}$ was found to have no effect on the rates of redox reactions.

Because the mechanisms of the reactions involved are not yet fully understood, the following interpretation of rate data should be regarded as preliminary.

The $k_{obs}(NiL1^{3+})/k_{obs}(NiL2^{3+})$ ratios for Ni(III) reduction were found to be strongly dependent on the nature of the substrate. For AH an approximately 6-fold acceleration of $[NiL2]^{3+}$ reduction as compared to $[NiL1]^{3+}$ reduction is observed. On the contrary, when AP is used as the substrate, the reduction of ditopic $[NiL2]^{3+}$ is approximately 50-fold slower than the reduction of the monomacrocyclic complex. We suggest, that in the former case, the supramolecular complex between the ditopic molecule and the substrate is formed. The formation of such a structure is followed by (or accompanied by) an electron transfer process that facilitates the overal redox reaction. This implies that the supramolecular complexes formed between $[NiL2]^{3+}$ and either β-AlaH$^+$ or AH, are structurally similar to one another. This conclusion seems quite resonable when one consider the similarities between the two substrates. The supramolecular complex involving $[NiL2]^{3+}$ and AP is apparently not formed, either because the crown ether interacts more weakly with aromatic ammonium ions than with aliphatic ammonium ions[23] or because the ditopic complex and the substrate are spatially incompatible. In any case, the presence of bulky substituents, like a benzocrown, in the nickel complex creates significant steric hindrance (at least from one side of the azamacrocycle) for interaction between reagents.

The observed rate constants measured at different temperatures (20 – 65°C) were plotted on Arrenius coordinates giving a straight line for each reaction. The activation parameters obtained in this way (Table 2) are difficult to interpret because the mechanism of the overall process is still unknown. It should be mentioned, however, that the difference between the monotopic complex and the ditopic complex decreases significantly with an increase of temperature (Table 2). This can be rationalized in terms of faster interconversion between the "open" and "closed" conformers of the ditopic complex at higher temperatures, with the redox behavior of "open" form of $[NiL2]^{3+}$ being similar to that of monotopic complex $[NiL1]^{3+}$.

Additional evidence for the hypothesis discussed above follows from the salt effect observed in the systems studied. The influence of 0.1 M $NaClO_4$ on the rates of $[NiL1]^{3+}$ reduction can be considered as a net ionic strength effect and causes an approximately 1.2-fold decrease of k_{obs} for both substrates. For $[NiL2]^{3+}$, complexation between Na^+ and the crown-ether subunit should be taken into account. On the one hand, this process would compete with substrate-receptor interaction, while, on the other hand, it would stabilize the "open" conformation of $[NiL2]^{3+}$. Apparently, the former effect plays a significant role in the case of AH (the reduction of $[NiL2]^{3+}$ is 1.5-fold slower in the presence of 0.1 M $NaClO_4$). The latter is evidently observed in the reaction of AP with $[NiL2]^{3+}$, where preliminary substrate-receptor complex formation is unlikely. The addition of $NaClO_4$, in this case, causes a 2-fold acceleration of the redox process. Consequently, one can see an allosteric effect in low-molecular weight systems based on $[NiL2]^{3+}$.

Table 2 The rates of reduction of nickel(III) complexes in acetonitrile solutions containing 0.01 M $HClO_4$ (25°C)

Reductant	*Ni(III)*	k_{obs},[a] *l/mol s*	$E^{\#}$, *kJ/mol*	*k(NiL1)/k(NiL2)*
m-Aminophenol (AP)	NiL1	7.6 (6.3)	43	47.5 (25°C)
	NiL2	0.16 (0.31)	64	24.5 (50°C)
β-Alanine hydrazide (AH)	NiL1	0.052 (0.041)	133	0.17 (25°C)
	NiL2	0.30 (0.19)	83	0.80 (50°C)

a The data given in parentheses were obtained in solutions containing 0.1 M $NaClO_4$.

CONCLUSION

It can be concluded from the experimental data that the presence of two different centers in one molecule provides new possibilities for the molecular design of systems with finely adjustable physico-chemical properties and reactivity. In particular, substrate interaction with the crown ether fragment of the ditopic molecule causes a shift in the Ni(III)/Ni(II) potential of the redox fragment of the same ditopic molecule. The shift is bigger in the case of bifunctional substrates which are capable of two-

centered binding with the ditopic complex. The formation of a supramolecular complex between the ditopic molecule and a bifunctional redox substrate may facilitate the reduction of Ni(III) (and, consequently, the oxidation of substrate). Spatial compatibility of reagents is necessary to facilitate this reaction pathway.

There is still much to be learned about these ditopic systems, and such investigations are currently under way in our laboratory.

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MATERIALS AND METHODS

Reagents

All reagents were of reagent grade. The acetonitrile used for electrochemical and kinetic measurements was distilled twice over P_2O_5. Ethanol was dried by distillation over Mg.

Syntheses

Caution! Some of the compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with care.

The β-alanine hydrazide was prepared by reaction of β-alanine ethyl ester with an excess of hydrazine hydrate in absolute ethanol.[24] The macrocyclic complex $[NiL1](ClO_4)_2$ was synthesized according to the method of Korybut-Daszkiewicz[12].

$[NiL2](ClO_4)_2$. A solution of 0.18 g (0.34 mmol) of $[NiL1](ClO_4)_2$ in 10 ml of absolute ethanol was added to a solution of 0.10 g (0.34 mmol) of formylbenzo-15-crown-5 in 10 ml of absolute ethanol. $HClO_4$ (0.34 mmol, 0.037 ml 9.18 M $HClO_4$) was then added to the resulting mixture. The solution obtained was refluxed under argon for 1.5 hrs. Dry benzene (0.5 ml) was then added. The ternary azeotrope H_2O-C_6H_6-EtOH was distilled off for 10 minutes. The reaction mixture was refluxed again for 1 hr and the addition af 0.5 ml of dry benzene and azeotropic distillation were repeated. After an additional 2-hour reflux the solution was cooled to room temperature. Further manipulations could be performed in an air atmosphere. A viscous yellow oil formed in several hours and was solidified by treatment with diethyl ether. The resulting yellow powder was filtered off, washed with diethyl ether and dried in the air. Yield: 0.12 g (40%). *Anal.* Calc. for $C_{28}H_{43}N_5Cl_2O_{13}Ni$: C,42.5; H, 5.8; N, 7.9%. Found: C,42.1; H, 5.3; N, 7.5%.

Instrumentation

Electronic absorption spectra were recorded on Specord M40 and Specord UV-Vis (Karl Zeiss) spectrophotometers. The IR spectra were obtained from KBr disks and Nujol mulls using a Specord 75 IR (Karl Zeiss) spectrometer. ESR spectra were measured using an E9 Varian (X-band) ESR system, with MnO magnetically diluted with MgO as a standard. Fast atom bombardment (FAB) mass spectra were obtained in a matrix of neat glycerol, argon was used as a fast atom beam.

Electrochemical measurements

Cyclic voltammetry (CV) was performed using a three-electrode system consisting of platinum working and auxiliary electrodes and a saturated calomel reference electrode (SCE). Voltammograms were generated with a PA-3 analyzer (Laboratorni pristroje, Praha). All measurements, unless otherwise stated, were performed in neutral aqueous solutions containing 0.1 M $NaClO_4$ or in acetonitrile solutions acidified with 0.01 M $HClO_4$ in the presence of 0.1 M $[(n\text{-}Bu)_4N]BF_4$ as a supporting electrolyte. The concentration of nickel complexes was 2.5×10^{-3} M. All the potentials throughout this paper were obtained at a sweep rate of 100 mV/s and are quoted *versus* SCE.

Kinetic measurements

The solutions of nickel(III) complexes were obtained by electrochemical oxidation of the corresponding nickel(II) complexes at 1.1 V. The kinetic studies were performed under pseudo-first order conditions with a large excess of substrate (the concentrations of nickel(III) were $(1\text{–}5)\times10^{-4}$ M, the concentrations of reductants were $(0.1\text{–}1)\times10^{-2}$ M). The redox reactions were followed spectrophotometrically using a two-beem instrument by the decrease of Ni(III) absorption at *ca.* 30000 cm^{-1} in the sample cell. The concentrations of all components in the reference cell were the same as those in the sample cell except that nickel(II) complexes were used in the reference cell in place of the nickel(III) compounds used in the reacting systems. This was necessary to adjust for the *ca.* 30 000 cm^{-1} absorption of organic components in the reaction mixture (mainly, the benzene ring of the crown ether).

All measurements were carried out in a thermostated (±0.1°C) quartz cell (1.0 cm). Solutions of reagents were thermostated for about 10 minutes before measurement. Unless otherwise stated all reactions were performed in

acetonitrile solutions containing 0.01 M $HClO_4$. The observed rate constants were calculated with an accuracy of about 15%; the accuracy in the determination of activation energies was ± 10 kJ/mol.

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