Polynuclear Oxalate-bridged Nickel Complexes based on Bis(macrocyclic) Building Blocks: Synthesis, Spectral and Electrochemical Studies

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Polynuclear Oxalate-bridged Nickel Complexes based on Bis(macrocyclic) Building Blocks: Synthesis, Spectral and Electrochemical Studies

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Several polymeric, oxalate-bridged supramolecular structures based on dinickel complexes of bis(macrocyclic) pentaaza ligands having a polymethylene or xylylene spacer between macrocyclic subunits were synthesized and characterized by means of UV VIS, IR spectroscopy and cyclic voltammetry. Electrochemical data reveal that bis(macrocyclic) amine ligands do not stabilize the nickel(III) oxidation state as effectively as does the related monomacrocycle. For most of the compounds studied, the stability of the mixed-valent Ni^{III}-Ni^{II} state relative to the isovalent ones (comproportionation equilibrium) does not depend on the structure of the spacer except for two complexes which display lower stability in this state. In the complex having the shortest dimethylene bridge, electronic interactions in the binuclear core may account for the observed effect while steric repulsions play an important role in the *m*-xylylene-bridged derivative.

INTRODUCTION

Azamacrocyclic metal complexes have been widely used in the construction of various types of supramolecular aggregates [1,2]. Bis(macrocycles) are an important subclass of azamacrocyclic ligands that are capable of binding pairs of transition metal ions. Typically in these compounds, two cyclic polyaza subunits are linked through an aliphatic or aromatic spacer that joins the two nitrogen atoms simultaneously coordinated to the metal ions [3,4] or by a covalent bond between two carbon atoms [5]. We have previously reported a method for the preparation of a new type of bis(macrocyclic) dinickel(II) and dicopper(II) complexes in which the 14-membered pentaaza units are linked by polymethylene or xylylene bridges via the non-coordinated nitrogen atoms [6,7].

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Another important class of binuclear amine complexes comprises compounds in which the two metal-amine subunits are bound by oxalate. This anion is a typical bridging ligand for nickel(II) amine complexes that facilitates effective electronic metal–metal interaction. Studies of the structural features, magnetic properties, and thermodynamic behavior of binuclear nickel complexes of this type are numerous [8–13], but only one complex, {[Ni(cyclam)]$_2$ox}$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane, ox^{2-} = oxalate anion) has been studied electrochemically [14]. We have recently investigated the electrochemical behavior of several other binuclear nickel(II)-oxalate complexes containing open-chained or monomacrocyclic amines as co-ligands [15].

In the present work, we examined compounds formed between the bis(macrocyclic) dinickel complexes and the oxalate anion. Such structures allowed us to combine the features of both types of binuclear species. These complexes exhibit variability due to differences in electronic and spatial relationships in the bridges between the macrocyclic subunits. We anticipated that the length and the nature of the spacer group would affect the electrostatic and electronic interactions between the metal centers. The present work was therefore dedicated to the syntheses of bis(pentaazamacrocyclic) dinickel complexes possessing polymethylene or xylylene spacers (Fig. 1) and the oxalate anion and their characterization by spectral and electro-
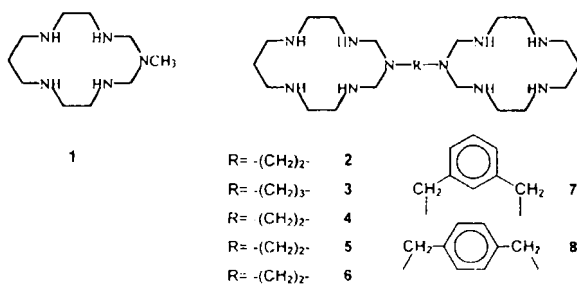
chemical methods. The goal was to examine the influence of the structure of bis(macrocyclic) ligands on the nature and the extent of metal–metal communication.

RESULTS AND DISCUSSION

Structure and Spectral Characteristics of Oxalate-bridged Complexes

Structural investigations revealed that the oxalate dianion in oxalate-bridged nickel amine complexes acts as a bis(bidentate) ligand [11–14,16]. Each nickel(II) ion in these compounds is coordinated by two oxygen atoms of the oxalate occupying neighboring (*cis*) positions and four nitrogen atoms. The amine exhibits a folded conformation (Fig. 2). The planarity of the fragment formed by two metal ions and the oxalate allows the most effective electronic interactions between cations and determines the steric arrangement of the amine components. No steric interaction between the ligands within the binu-

FIGURE 1   Mono- and bis(macrocyclic) ligands used for the preparation of oxalate-bridged nickel complexes.
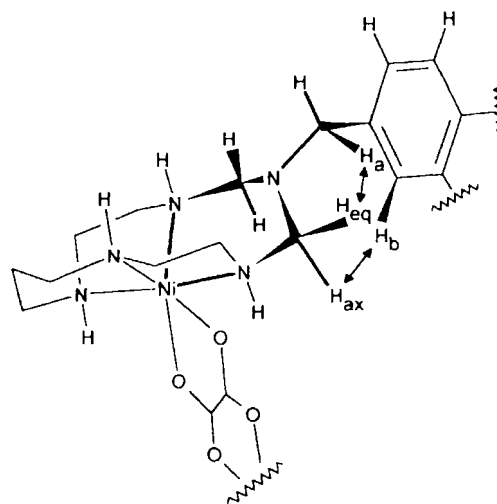

FIGURE 2   The sketch of an half of oxalate-bridged core showing possible intramolecular repulsions between the hydrogen atoms (the conformation of the macrocycle is taken from the crystallographic data [16], the 6-membered metallocycle is shown by bold).

clear core is observed in complexes formed by open-chained or monomacrocyclic amines. This intramolecular interaction may be significant, however, in the oxalate-bridged bis(macrocyclic) compounds where two sources of steric repulsion could be expected.

One type of steric interaction may arise from the repulsion of the equatorially oriented hydrogen atom of methylene group of one 6-membered metallocycle and that of the spacer (H_{eq}-H_a in Fig. 2). In addition, in xylylene-bridged complexes the repulsion between axially oriented hydrogen atom of chelate ring and the aromatic ring hydrogen (H_{ax}-H_b in Fig. 2) is also highly probable. Interactions of this type can result in a deviation of the 6-membered metallocycle from its energetically most stable arrangement.

Since the two macrocyclic subunits in this bis(macrocyclic) compounds are no longer structurally independent this may lead to the appearance of a second potential source of nickel coordination polyhedron deformation. The structure of the complex is probably influenced by both the conformational possibilities of the spacer and the stereochemical demands of oxalate bridging ligand. This means that in the systems under consideration a deviation of the $Ni_2(ox)$-fragment from planarity could be observed and such a deformation should influence the electronic metal–metal interaction in the complexes.

A single structure, an oxalate-bridged dimer A (Fig. 3), is possible for monomacrocyclic complexes, but three structural types must be considered for bis(macrocyclic) compounds. These are: (i) intermolecular $n + n$ polymeric structure B in which oxalate binds monomacrocyclic subunits of different bis(macrocyclic) molecules; (ii) intramolecular $2 + 2$ aggregates C; (iii) intramolecular $1 + 1$ structure D with oxalate ion bridging monomacrocyclic subunits of the same bis(macrocyclic) molecule. The formation of a particular structure will be determined by the nature of the bridge linking two macrocyclic fragments and only the formation of a type D

structure will depend on geometrical complementarity between the reaction partners.

In other words, structure D can be formed only if the spacer is long enough to accommodate the oxalate with simultaneous folding of the macrocycles. Structural study of $[(NiL)_2ox](ClO_4)_2$ (L = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexa-zacyclotetradecane) has shown [16] that the hydroxyethyl substituents of the folded macrocycles in this complex are directed inside the binuclear core; the distance between oxygen atoms of the substituents is 6.9 Å. Taking this as a model for bis(macrocyclic) oxalate compounds, only $[Ni_26]^{4+}$ is a candidate for the formation of structure D. For compounds having shorter spacers, both type B and C structures are possible. In the latter cases, their formation may be accompanied by differing degrees of ligand strain depending on the bridge.

Unfortunately, we were unable to obtain any direct evidences regarding the structure of oxalate compounds in solutions. The FAB mass-spectra (Ar atoms, 5 keV) of $[Ni_22(ox)](ClO_4)_2$ and $[Ni_24(ox)](ClO_4)_2$ showed no peaks up to m/z ≤ 1500. This indicates the absence of type D complexes in the matrix. When the sample of $[Ni_24(ox)](ClO_4)_2$ was subjected to enough energy to break the Ni-O (oxalate) bond (Cs^+, 10 keV), three peaks in the mass spectrum: m/z 775, 1650,
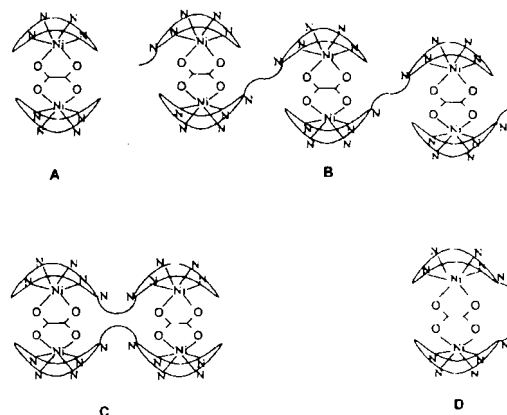

FIGURE 3 Schematic presentation of the possible structures of oxalate-bridged polynuclear compounds.

and 2526 (traces) were registered. The formulas $\{[Ni_24(ox)]ClO_4\}^+$, $\{[Ni_24(ox)]_2 (ClO_4)_3\}^+$ and $\{[Ni_24(ox)]_3(ClO_4)_5\}^+$ were assigned to these peaks. Formally these values correspond to the structures **D**, **C** and **B** with one perchlorate anion abstracted. Of course, these are gas phase rather than solution data. Note that the species formed by the cleavage of both Ni-O(oxalate) coordination bonds (*i.e.*, containing the bis(macrocyclic) fragment with one $NiN_4(ox)$ and one NiN_4 polyhedrons) will have the same *m/z* as **D** but a different structure. The spectral and electrochemical behaviour of the complexes studied (*vide infra*) suggest that they have similar structures (either **B** or **C**) although structure **B** seems to us more probable. In the subsequent text the formulas $[Ni_2L(ox)](ClO_4)_2$ (L = 2 – 8) will be used for simplicity assuming that Ni_2L means two analogous oxalate-bridged macrocyclic units but originated from *different* bis(macrocyclic) molecules. Despite similar structures, one would expect spacer-dependent differences in the deformation of nickel(II) coordination sphere for the oxalate-bridged complexes.

The complexes obtained were characterized by the IR and UV-Vis techniques (see Materials and Methods). The IR spectra of all compounds are very similar and do not differ significantly from the spectra of related complexes with the oxalate bridging ligand [8,9]. Three bands observed in the UV-Vis spectra are characteristic for the spin-allowed transitions of d^8electronic configuration in the pseudo-octahedral ligand field of a *cis*-NiN_4O_2-chromophore [17].

In general, spectral characteristics of the complexes show no definite dependence on the structure of the spacer. The only parameter standing out is essentially larger value of the molar absorption coefficient ε of the high energy band in complex with *m*-xylyene bridged ligand **7**. Assuming that the lowering of the symmetry of the metal chromophore will result in an increase in ε, this allows to suggest that the nickel ion in this compound possesses the most

deformed environment. Such an assumption agrees with the redox properties of this complex (*vide infra*).

Electrochemical Properties of the Complexes

The electrochemical properties of the oxalate-bridged nickel compounds were studied by cyclic voltammetry (CV) in three solvents-DMSO, DMF and acetonitrile (MeCN). Analogously to binuclear oxalate complexes with mono-macrocyclic amines [14,15], two consecutive redox processes are characteristic for all the bis (macrocyclic) compounds. This clearly demonstrates that each oxalate-bridged dimetallic subunit in these compounds behaves independently and experiences rather little influence of neighboring one. Therefore, the redox process at less positive potentials can be treated as arising from the oxidation of one metal(II) center in binuclear unit leading to the mixed-valence $(Ni^{III}-Ni^{II})$ product. The second process can be ascribed to the oxidation of another nickel(II) ion in the mixed-valence fragment giving the $(Ni^{III}-Ni^{III})$ species.

The electrochemical behavior of the oxalate-bridged compounds was studied in DMSO solutions containing $ca.1 \times 10^{-3}$M of the complexes (as an example, the CV curve for $[Ni_23(ox)](ClO_4)_2$ is shown in Fig. 4a). Both redox transformations in this solvent are quasi-reversible with the better reversibility of the first process. Such a peculiarity is also characteristic [15] for oxalate complex of the monomacrocyclic analogue **1**. The formal potentials of E_f of redox transformations calculated as midpoints between corresponding anodic and cathodic peaks show distinct dependence on the structure of macrocycle (Tab. I).

Thus, the values of E_{f1} and E_{f2} for $[Ni1_2(ox)]^{2+}$ are lower than those for all bis(macrocyclic) complexes. This means that the assessments of the higher oxidation state of metal are easier from the thermodynamic point of view in
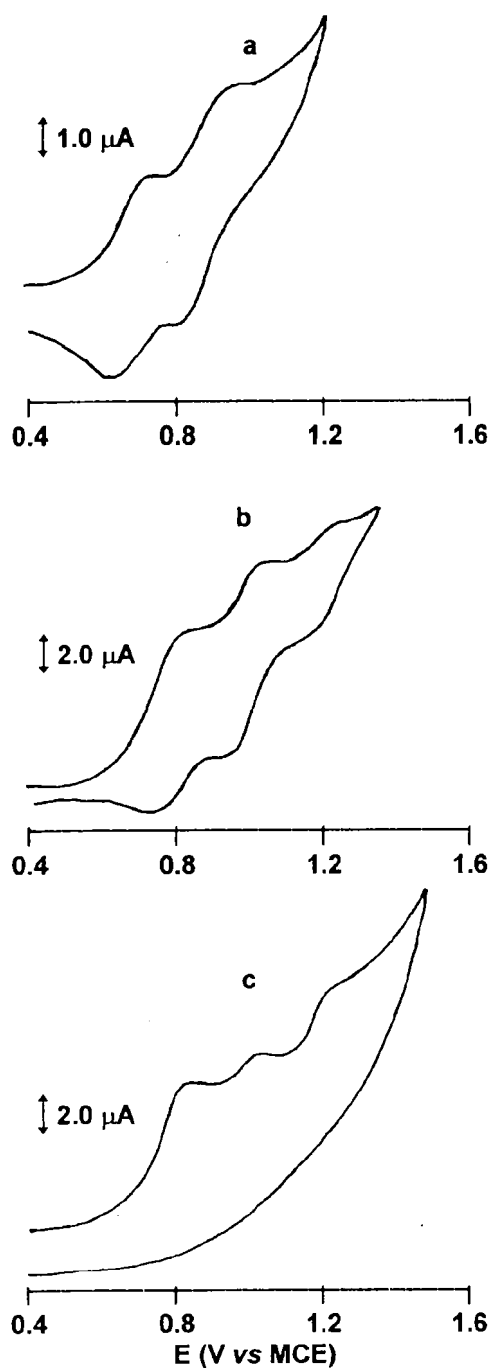
FIGURE 4 Cyclic voltammograms at a GC electrode at scan rate 50 mV/s of the complexes: (a) $[Ni_23(ox)](ClO_4)_2$ in DMSO containing 0.1 M Na-p-Ts ($C_{complex} = 1.0 \times 10^{-3}$ M); (b) $[Ni_23(ox)](ClO_4)_2$ in MeCN containing 0.1 M $[Bu_4N][BF_4]$ ($C_{complex} = 1.0 \times 10^{-3}$ M); (c) $[(Ni1)_2ox](ClO_4)_2$ in MeCN containing 0.1 M $[Bu_4N][BF_4]$ ($C_{complex} = 5.0 \times 10^{-4}$ M).

TABLE I Electrochemical parameters (mV vs. MCE) for the stepwise redox processes in nickel oxalate-amine complexes $[Ni_2L(ox)]^{2+}$ in DMSO (upper values) and DMF (lower values) both containing 0.1 M Na-p-TS at 25°C

Amine L	E_{f1}	E_{f2}	$\Delta E_f = E_{f2} - E_{f1}$	$K_{com} \times 10^{-3}$
1[a]	585 (70)[b]	810 (120)	225	6.4 ± 0.9
	580 (60)	795 (85)	215	4.3 ± 1.2
2	630 (65)	790 (80)	160	0.5 ± 0.3
	_c	_c	_c	_c
3	635 (90)	835 (110)	200	2.4 ± 0.5
	610 (80)	810 (80)	200	2.4 ± 0.9
4	635 (70)	840 (120)	205	2.9 ± 0.6
	590 (80)	790 (80)	200	2.4 ± 0.9
5	630 (100)	830 (110)	200	2.4 ± 0.5
	560 (80)	760 (80)	200	2.4 ± 0.9
6	635 (70)	835 (90)	200	2.4 ± 0.5
	585 (70)	795 (90)	210	3.5 ± 1.1
7	685 (90)	865 (90)	180	1.1 ± 0.2
	640 (100)	815 (80)	175	0.9 ± 0.4
8	640 (100)	835 (120)	195	2.0 ± 0.4
	615 (70)	820 (80)	205	2.9 ± 1.0

[a] Data for complex $[(Ni1)_2ox](ClO_4)_2$ are taken from Ref. [15].
[b] The separation of anodic and cathodic peaks in mV is given in parentheses.
[c] Insufficiently soluble.

complex of monomacrocyclic ligand. It is well established [18] that the transformation of nickel(II) to nickel(III) is accompanied by essential changes in the Ni-donor atoms distances and, to some extent, in the conformation of the macrocycle. Such structural changes are expected to be more energy-consumable for bis(macrocyclic) complexes as compared to monomacrocyclic one and can lead to the appearance of additional intramolecular repulsion in the former case.

As an argument confirming the existence of such interactions serve the E_f values for complexes of xylylene-bridged ligands 7 and 8. As it was shown [19], the redox potential of $Ni^{III/II}$ couple in dinickel complexes of bis(macrocyclic) ligands linked via coordinated nitrogen atom becomes higher when the polymethylene bridge is replaced by m- or p-xylylene one. This was explained by inductive effect of aromatic spacer which reduces the donor strength of the tertiary nitrogen atom thus leading to the destabilization of the higher oxidation state. Analogous

mechanism has little if any importance in the oxalate complexes under consideration because there is no direct bond between nickel(II) and the bridge-head nitrogen atom. Indeed, the redox processes in *p*-xylylene derivative $[Ni_28(ox)]^{2+}$ take place at the same potentials as for poly-methylene-linked complexes. At the same time, the compound with *m*-xylylene bridge (in which the repulsion between hydrogen atoms of aro-matic spacer and those of 6-membered chelate rings was suggested based on spectral data) is characterized by higher values of E_f.

The complex $[Ni_22(ox)]^{2+}$ drops out also of the series of bis(macrocyclic) compounds: the E_{f1} value for this complex is the same as for other polymethylene-bridged compounds while E_{f2} is the lowest. Assuming that the presence of positive charge in close proximity of redox active center destabilizes the higher oxidation state due to electrostatic interactions [19], one can expect that the mutual destabilizing influ-ence of the neighboring $[Ni^{III}Ni^{II}2(ox)]^{3+}$ units will be the largest (and the E_{f2} value the highest) just in this compound with the shortest bridge. Quite opposite effect observed allows to suggest that an electrostatic term is more than compen-sated by another factor having an electronic nature. Apparently, in contrast to other com-pounds the oxidation of the first metal ion in $[Ni_2^{II}2(ox)]^{2+}$ binuclear core results not only in the conformational changes in amine molecule but is also accompanied by essential structural changes in $Ni_2(ox)$-fragment thus making the assessment of $[Ni_2^{III}2(ox)]^{4+}$ much easier.

The electrochemical study of oxalate com-plexes was also performed in DMF solutions containing *ca.* $(3 \div 5) \times 10^{-4}$ M of the complexes. Due to the insufficient solubility of complex $[Ni_22(ox)](ClO_4)_2$ reliable values of its redox parameters were not obtained. The behaviour of other complexes in DMF is similar to that in DMSO (Tab. I) though the difference between complexes of monomacrocyclic and bis(macro-cyclic) amines is not so pronounced in the former case. Similar effect of these solvents has been

observed previously for other azamacrocyclic oxalate complexes [15]. The variations of E_f in DMF are independent on the structure of the macrocycles except for $[Ni_27(ox)]^{2+}$ for which the values of E_f of both redox transformations are higher than for other complexes.

The electrochemical characteristics of oxalate-bridged compounds were also obtained in MeCN. Typical concentration of the complexes in mea-surements was *ca.* 5×10^{-4} M, however, the xylylene-bridged compounds were practically insoluble while $[Ni_22(ox)](ClO_4)_2$ decomposes in this solvent. The redox behavior of the remaining complexes differs from that observed in DMSO or DMF. In MeCN three processes with $E_{f1} = 805$ mV, $E_{f2} = 1005$ mV and $E_{f3} = 1215$ mV were registered for all the compounds (as an example, the CV curve for $[Ni_23(ox)]^{2+}$ is presented in Fig. 4b). Noteworthy, the oxalate complex of the mono-macrocycle 1 is also oxidized in three steps, though irreversibly (Fig. 4c). Analogously to the solutions in DMSO and DMF, first two redox transformations (characterized by E_{f1} and E_{f2}) are explained by the stepwise oxidation-reduction of nickel centers in oxalate-bridged fragments. The formal potentials potentials in MeCN show no influence on the structure of the amine ligands. The appearance of the additional redox process at higher potential both for mono- and bis(macro-cyclic) complexes necessitates more detailed discussion.

Obviously, the dissociation of oxalate com-plexes must be taken into consideration as the most probable chemical reaction in this solvent. It was shown [14] that in aqueous solution the corresponding nickel cyclam complex dissoci-ates to the mononuclear nickel(II) species *cis*-$[Ni(cyclam)(Solv)_2]^{2+}$ (Solv = H_2O) with amine possessing a folded conformation. The content of *cis*-$[Ni(cyclam)(Solv)_2]^{2+}$ in water is relatively high but in DMSO and DMF it is negligible and can be raised only by the addition of acid [14,15]. At the same time, MeCN is known as a specific coordinating solvent for nickel amine complexes [20] and it is quite reasonable to expect

that its molecules will effectively substitute the bridging oxalate leading to the presence in this solvent of an essential amount of redox active fragments with cis-[NiL(MeCN)$_2$]$^{2+}$ structure. Therefore, one can assume that the redox transformation exactly of these species is responsible for the appearance of the third process with E_{f3} at ca. 1215 mV. Though this value seems to be relatively high for Ni$^{III/II}$ couple in tetraamine environment [18], it is quite explainable remembering that it is related to the complex in which the macrocycle possesses a folded conformation. As has been shown [15], the differences of E_f between cis- and trans-Ni$^{III/II}$L^1(Solv)$_2$ couples are ca. 270 mV both in DMF and DMSO. Using the value of the potential for trans-[Ni^{III}/^{II}L^1(MeCN)$_2$] (E_f ca. 915 mV [21]) one can calculate very close difference for MeCN solution (ca. 300 mV).

Comproportionation Equilibria

Comproportionation constants of binuclear compounds characterize the equilibrium

$$[Ni^{II} - Ni^{II}]^{2+} + [Ni^{III} - Ni^{III}]^{4+} \Leftrightarrow 2[Ni^{III} - Ni^{II}]^{3+}$$

$$(1)$$
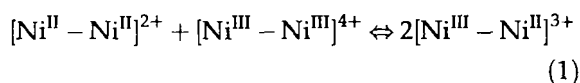
and are determined by the values of E_{f1} and E_{f2} according to Eq. (2)

$$K_{com} = \exp[(E_{f2} - E_{f1})F/RT]$$

$$(2)$$

As follows from Table I, in DMSO and DMF the monomacrocyclic complex reveals the highest stability of the mixed-valence state relative to the isovalent ones. The values of K_{com} for bis (macrocyclic) complexes are lower and remain nearly constant, except that for [Ni$_2$2(ox)]$^{2+}$ and [Ni$_2$7(ox)]$^{2+}$. Though the stability of the mixed-valent states in two latter complexes is lower, the factors causing this are different: a smaller value of ΔE_f for [Ni$_2$2(ox)] is determined by lower value of E_{f2}, while for [Ni$_2$7(ox)]-mainly by more positive value of E_{f1}. This indicates different contributions of structural and electronic terms in the K_{com} of these complexes.

The values of ΔE_f ca. 200 mV ($K_{com} = (2.4 \pm 0,9) \times 10^3$) in MeCN are almost the same as in other media thus indicating the negligible effect at least of these three solvents on the comproportionation equilibria. Such an observation agrees well with our data concerning the oxalate complexes of monomacrocyclic azacyclams [15].

CONCLUSIONS

The data obtained indicate that the bis(macrocyclic) dinickel(II) complexes and the oxalate ion form polymeric supramolecular structures in which the binuclear cores are linked with polymethylene or xylylene bridges. Irrespective of the structure of the bridges, the complexes show similar spectral characteristics. The only exception is the compound with m-xylylene bridge in which some distortion of the metal coordination polyhedron can be suggested based on higher value of molar absorption coefficient of d–d band.

Amine bis(macrocyclic) ligands in the oxalate-bridged complexes exert less stabilizing effect on nickel(III) oxidation state as compared to the related monomacrocycle. For the majority of compounds the stability of the mixed-valent Ni^{III}–Ni^{II} state relative to isovalent one (comproportionation equilibrium) does not depend on the structure of the bis(macrocycle). The lower stability of this state in [Ni$_2$2(ox)] with the shortest bridge can be accounted for by an electronic effect while in m-xylylene derivative [Ni$_2$7(ox)] an intramolecular steric interactions may play an important role.

The nature of the solvent exerts rather small effect on comproportionation equilibria but influences electrochemical behavior of the complexes as a whole. Thus three redox processes are observed in MeCN in contrast to two ones registered in DMSO and DMF. This peculiarity is connected with the essential dissociation of oxalate complexes in the former solvent leading to the formation of cis-[NiL(MeCN)$_2$]$^{2+}$ fragments

which redox transformation takes place at more positive potentials.

MATERIALS AND METHODS

Syntheses

The dinickel complexes $Ni_2L(ClO_4)_4$ (L = 2 – 4) was synthesized as described in [6]. The preparation of dinickel complexes with 5 – 8 were carried out analogously using 1,6-hexanediamine, 1,10-decanediamine, 1,3- and 1,4-xylylenediamine, respectively [21]. Complex $[(Ni1)_2ox](ClO_4)_2$ was obtained as described in [15].

The following general procedure was used for the preparation of macrocyclic oxalate-bridged compounds.

To the solution of 1.0 mmol of the starting dinickel complex $Ni_2L(ClO_4)_4$ in $30\,cm^3$ of water was added 1.0 mmol of potassium oxalate monohydrate dissolved in $20\,cm^3$ of water pH of the solution was adjusted to 8 with aqueous NaOH. Gentle heating of the solution at 50°C during 2 h with stirring resulted in the change of the color from yellow to wine-red with simultaneous formation of pink – violet precipitate. After cooling it was filtered off, washed with water, then with ethanol and dried in vacuum-desiccator over P_4O_{10}. The yields of dinickel complexes were ca. 80%. Because of the low solubility of the products we were unable to recrystallize them from common solvents but the microanalytical data confirm their purity and correspond to the general formula $Ni_2L(ox)(ClO_4)_2$.

$[Ni_22(ox)(ClO_4)_2 \cdot$ Calc. for $C_{22}H_{50}Cl_2N_{10}Ni_2$ O_{12}: C 31.6; H 6.0; N 16.8%.

Found: C 31.7; H 6.1; N 16.9%. UV-Vis in DMSO (λ, nm; (molar absorption coefficients ε $M^{-1}cm^{-1}$, per one nickel ion): 338 sh, 538 (15), 838 (16).

$[Ni_23(ox)](ClO_4)_2 \cdot$ Calc. for $C_{23}H_{52}Cl_2N_{10}$ Ni_2 O_{12}: C 32.5; H 6.2; N 16.5%.

Found: C 32.7; H 6.3; N 16.6%. UV-Vis: 336 (64), 537 (28), 846 (21).

$[Ni_24(ox)](ClO_4)_2 \cdot$ Calc. for $C_{25}H_{54}Cl_2N_{10}Ni_2$ O_{12}: C 34.3; H 6.2; N 16.0%.

Found: C 34.4; H 6.3; N 16.1%. UV-Vis: 339 (61), 539 (28), 840 (19).

$[Ni_25(ox)](ClO_4)_2 \cdot$ Calc. for $C_{26}H_{56}Cl_2N_{10}Ni_2$ O_{12}: C 35.1; H 6.3; N 15.7%.

Found: C 35.2; H 6.1; N 15.9%. UV-Vis: 332 (78), 537 (25), 847 (20).

$[Ni_26(ox)](ClO_4)_2 \cdot$ Calc. for $C_{30}H_{64}Cl_2N_{10}Ni_2$ O_{12}: C 38.2; H 6.8; N 14.8%.

Found: C 38.3; H 6.5; N 14.9%. UV-Vis: 334 (52), 538 (21), 837 (21).

$[Ni_27(ox)](ClO_4)_2 \cdot$ Calc. for $C_{28}H_{52}Cl_2N_{10}Ni_2$ O_{12}: C 37.0; H 5.8; N 15.5%.

Found: C 37.1; H 6.1; N 15.6%. UV-Vis: 333 (110), 534 (31), 847 (22).

$[Ni_28(ox)](ClO_4)_2 \cdot$ Calc. for $C_{28}H_{52}Cl_2N_{10}Ni_2$ O_{12}: C 37.0; H 5.8; N 15.5%.

Found: C 37.2; H 6.0; N 15.6%. UV-Vis: 334 sh, 539 (21), 850 (14).

All complexes show very similar IR spectra with $\nu_{as}(O—C—O)$ at $1630\,cm^{-1}$ (strong), $\nu_s(O—C—O)$ at $1300\,cm^{-1}$ (weak) and $\nu_\delta(O—C—O)$ at $780^{-1}\,cm^{-1}$ (medium), $\nu(ClO_4)$ at ca. 1100 (very strong) and $625\,cm^{-1}$ (medium), ν_{as} (NH) at $3180\,cm^{-1}$ (medium) and ca. $3270\,cm^{-1}$ (shoulder).

Spectral Measurements

Infrared spectra of the complexes were recorded on a Nicolet FTIR-410 or Specord 75-IR spectrophotometers as KBr pellets. The electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer equipped with 1-cm cells thermostated at 25 ± 0.5°C. The fast atom bombardment (FAB) mass-spectra were measured on a spectrometer MX-1310 in glycerol using Ar atoms having the energy of ca. 5 keV or on AMD-604 mass spectrometer in *m*-nitrobenzyl alcohol under the bombardment with Cs^+ ions with the energy of 10 keV.

Electrochemical Measurements

The redox properties of oxalate complexes were studied by means of cyclic voltammetry in the

argon atmosphere at a glassy carbon (GC-20) electrode in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) both containing 0.1 M sodium p-toluenosulfonate, Na-p-Ts, as supporting electrolyte. This electrolyte is insoluble in acetonitrile (MeCN), therefore $[Bu_4N][BF_4]$ (0.1 M) was used for measurements in this solvent. All experiments were carried out in a three-electrode system at $25 \pm 0.5°C$. A 1 M NaCl aqueous calomel electrode (MCE) was used as a reference. It was connected to the electrolytic cell *via* an intermediate vessel, filled with the solution under investigation. The counter electrode was a Pt plate. The ferrocene/ferrocenium ion (Fc/Fc^+) redox couple was used as internal reference. It displayed one electron reversible wave centered at 0.415 V in DMF containing 0.1 M Na-p-Ts, 0.375 V in DMSO containing 0.1 M Na-p-Ts, and 0.580 V in MeCN containing 0.1 M $[Bu_4N][BF_4]$, respectively. All procedures used for cleaning of the GC electrode and the purification of solvents (Merck) were the same as described in [15]. The accuracy in determination of E_f was ± 5 mV in DMSO and ± 10 mV in DMF and MeCN.

Acknowledgements

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