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Formation of Nickel(III) Complexes with *n*-Dentate Amine Macrocycles ($n = 4, 5, 6$). ESR and Electrochemical Studies

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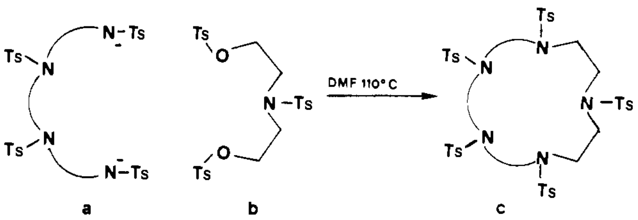
Low-spin nickel(III) complexes with the complete series of 12- to 16-membered cyclic tetraamines, with the novel series of 15- to 17-membered cyclic pentaamines, and with the 18-membered cyclic hexaamine have been prepared in acetonitrile solution by anodic and/or chemical oxidation of the corresponding Ni(II) complexes. Spin state and stereochemistry of the Ni(III) complexes have been deduced from the ESR spectra of the frozen solutions (77 K). The half-wave potential values, $E_{1/2}$, associated to the 2+/3+ quasi-reversible redox change in the considered complexes have been obtained through voltammetry experiments at a platinum electrode. $E_{1/2}$ values show that for tetraamine complexes the attainment of the Ni(III) state is easiest with the 14-membered macrocycle and is dramatically affected by contraction or expansion of the ligand cavity. This ring-size-dependent redox selectivity is drastically reduced in the complexes with pentadentate macrocycles. The synthesis of this novel series of cyclic pentaamines is described in detail.

Introduction

The incorporation of a metal ion into a tetraaza macrocyclic framework makes possible the access to unusually high oxidation states, which may be forbidden to the solvated cation or to complexes with noncyclic ligands. A well-known example is that of trivalent nickel.[1-6] This interesting behavior results from the unique combination of two properties of cyclic ligands: (i) formation of strong in-plane metal–nitrogen interactions, which raise the energy of the antibonding orbital (essentially metallic in character) from which the electron has to be removed in the oxidation process (this should be considered a *thermodynamic effect*); (ii) trapping of the strongly oxidizing metal cation in a closed framework, which reduces its tendency to react with the solvent or with uneliminated dissolved impurities (*kinetic effect*). Essentially due to this latter feature, the Ni^{II}/Ni^{III} redox couple in macrocyclic systems gives in general reversible or quasi-reversible responses, in an electrochemical sense; therefore, the $E_{1/2}$ values obtained from voltammetric investigations approach $E°$ values and reflect the relative thermodynamic stability of the trivalent state of nickel. Another intriguing feature that derives from point ii is the possibility of physical characterization of the solution-persistent Ni^{III} complex species. Busch and coworkers[5] were the first to measure the ESR spectra of a series of 14-membered tetraaza macrocyclic complexes obtained, in acetonitrile solution, through controlled-potential electrolysis; the spectra were those expected for a low-spin d^7 cation in a tetragonal environment, showing unambiguously the authenticity of the Ni^{III} oxidation state. On the other hand, "macrocyclic property" i implies that changes of the coordinating ability of the ligand should result in a change of the potential of the Ni^{II}/Ni^{III} redox couple. This point has been clearly demonstrated by Busch and associates, who considered complexes with ligands differing in the degree of unsaturation and/or the presence of substituents on the carbon backbone.[5] Electrochemical studies showed that the easiest oxidation to +3 occurred with the fully saturated, unsubstituted 14-membered tetraaza macrocycle, whereas progressive unsaturation and/or alkylation of the ring made progressively more difficult the attainment of the Ni^{III} state.

Scheme I



In the present work we want to consider to what extent the Ni^{II}/Ni^{III} redox change may be affected by a different type of modification of the coordinative framework: (a) the increase of the number of nitrogen donor atoms (to 5 and 6, in penta- and hexaaza macrocycles, respectively); (b) the control of the size of the macrocyclic cavity. For this purpose, we have studied the formation of nickel(III) complexes with (1) the complete series of fully saturated, unsubstituted 12- to 16-membered tetraaza macrocycles (ligands **1**–**6**, in Figure 1); (2) a novel series of saturated, unsubstituted pentaaza macrocycles (**7**–**9**), for which the synthesis is described in detail, and (3) the hexaaza macrocycle **10**.

The $Ni(macrocycle)^{2+}/Ni(macrocycle)^{3+}$ redox process has been investigated by voltammetric techniques in acetonitrile solution using platinum electrodes. The stereochemistry and the spin state of the Ni^{II} species in solution have been inferred from electronic spectra (and from magnetic moments of the solid complexes). The Ni^{III} complex species were obtained through chemical oxidation (using $NOBF_4$) and in some cases also through exhaustive electrolysis at a controlled potential. The spin state and the stereochemistry of the Ni^{III} complexes were inferred from ESR spectra of their frozen acetonitrile solutions.

The aim of this work is to interpret electrochemical data (the trend of $E_{1/2}$) in terms of the coordinative features (stereochemistry and metal–ligand interactions in the considered complexes). A preliminary account on the electrochemical behavior of the pentaaza macrocyclic complexes has been reported.[7]

Experimental Section

Synthesis of the Ligands and of Their Nickel(II) Complexes. Tetraaza macrocycles, with the exception of **3** and **5**, were obtained by synthetic routes based on the general procedures of Richman and Atkins,[8] and preparative details have been reported elsewhere (**1**, ref 8; **2**, ref 9; **4**, ref 6; **6**, ref 10). Their nickel(II) complexes were

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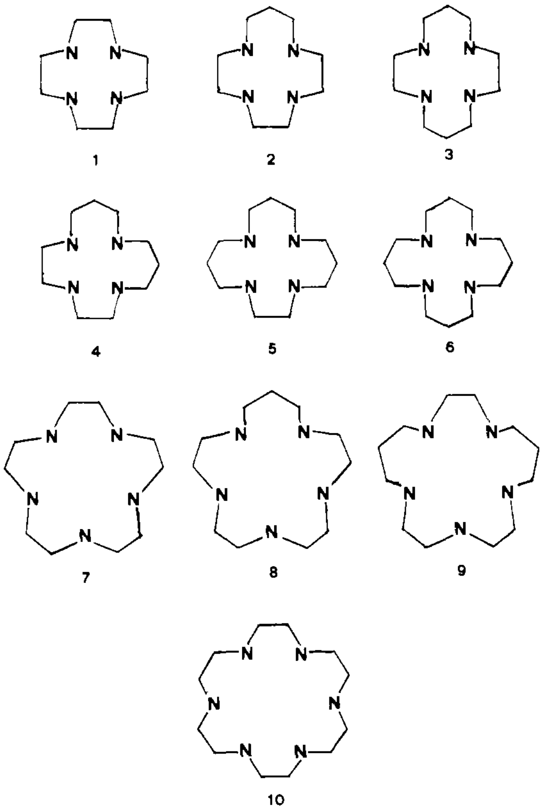

Figure 1. Cyclic polyamines studied in this work. Nomenclature: **1**, [12]aneN_4; **2**, [13]aneN_4; **3**, *sym*-[14]aneN_4; **4**, *asym*-[14]aneN_4; **5**, [15]aneN_4; **6**, [16]aneN_4; **7**, [15]aneN_5; **8**, [16]aneN_5; **9**, [17]aneN_5; **10**, [18]aneN_6.

obtained as perchlorates by mixing equimolar amounts of hot ethanolic solutions (5×10^{-2} M) of the metal salt and of the ligand. The yellow, diamagnetic complexes were recrystallized from water or methanol. Nickel(II) perchlorate complexes of **3** and **5** were obtained by the template procedure described by Barefield.[11]

Pentaaza Macrocycles (7–9). The synthesis of the quinquedentate macrocycles **7–9** is based on the condensation of the appropriate tosylated segments, as depicted in Scheme I (Ts = tosyl = *p*-toluenesulfonyl). Compound b was obtained and purified as previously described.[9] Preparation of species a involved the following processes.

(i) The linear aliphatic tetraamine was tosylated. In a typical preparation, 0.26 mol of the tetraamine (2,2,2-tet, 2,3,2-tet, or 3,2,3-tet; *m,n,p*-tet indicates a molecule having the formula $NH_2(CH_2)_mNH(CH_2)_nNH(CH_2)_pNH_2$) and 1.04 mol of NaOH were dissolved in 300 mL of water, in a 2-L round-bottomed flask. Tosyl chloride (200 g), dissolved in 750 mL of ether, was added dropwise under vigorous stirring over a period of 3–4 h. When the addition was complete, stirring was continued for 1 h. The precipitate, separated by filtration, was then suspended (not dissolved) in 0.5 L of ethanol, and the suspension was refluxed for 1 h. A crystalline white solid was obtained, which gave satisfactory elemental analysis. If desired, a true recrystallization can be performed with use of a very large volume of methanol. Refluxing in ethanol or recrystallization from methanol is not effective with the 2,3,2-tet derivative, for which a gummy substance is obtained in each case. Yields ranged from 50 to 70%.

(ii) Dianion a was not isolated, for instance, as a solid disodium salt, but was obtained in DMF solution, to be used in the cyclization step. In a typical synthesis, 0.10–0.15 mol of the tetratosylated tetraamine was dissolved in 1 L of anhydrous DMF (freshly distilled under vacuum from CaH_2), in a nitrogen atmosphere. To the vigorously stirred solution, a large excess of NaH (0.8–1.2 mol, suspended in oil) was added in small portions over a period of 2–3 h. Stirring was then continued for 4 h. The solution was filtered, in a stream of nitrogen through a sintered-glass frit, to remove unreacted NaH, directly into the round-bottomed flask in which the cyclization step was carried out.

Cyclization Step. To the previous solution, at 110 °C, was added dropwise, under stirring, 500 mL of a solution of compound b (equivalent amount) in DMF over a period of 2–3 h. Heating and stirring were maintained for a further 4 h. The cooled yellow solution was then rotovaporated to about 200 mL; during concentration, precipitation of a white solid, mostly NaOTs, occurred. Small amounts of the tosylated macrocycle, which also precipitated, were extracted with hot $CHCl_3$. The concentrated solution was dropped in 1.5 L of water with stirring, and a white noncrystalline precipitate formed. It was filtered off and dissolved in 2 L of hot $CHCl_3$. This solution, kept overnight on Na_2SO_4, was rotovaporated to 200–300 mL, and then 1 L of hot ethanol was added slowly; on cooling a crystalline white solid formed. Purity of the pentatosylated pentaamines was monitored by the C, H, N analysis and by the intensity of the stretching N–H band (at 3300 cm^{-1}). This band, which was present in the nonpurified product (due to the presence of unreacted tetraamine), completely disappeared after recrystallization in $CHCl_3/C_2H_5OH$. The yield of the cyclization step, based on the open-chain tosylated tetraamine, ranged within 50–80%.

Hydrolysis of the Pentatosylated Macrocycles and Extraction of the Cyclic Pentaamines. The pentatosylated macrocycle (70–90 g) was dissolved in 300 mL of 96% sulfuric acid and maintained under stirring at 100–110 °C for 3–4 days. To the dark-brown solution, cooled on an ice bath, were added slowly, with stirring, 1 L of ethanol and then 0.5 L of ether. A brownish precipitate formed, presumably the sulfate of the pentaprotonated ligand, which was filtered off on a glass frit and then dissolved in an ice-cooled 6 M NaOH solution (200 mL). Typically, 10 extractions with 200-mL portions of chloroform were performed. The $CHCl_3$ solution, desiccated over Na_2SO_4, was rotovaporated and then flashed off to leave a whitish yellow semisolid, which was recrystallized from 50–100 mL of anhydrous ether. In the case of [15]aneN_5 (mp 92 °C) and [16]aneN_5 (mp 94 °C) white needles were obtained. Anal. Calcd for [15]aneN_5, $C_{10}H_{25}N_5$: C, 55.77; H, 11.70; N, 32.52. Found: C, 55.15; H, 11.73; N, 32.07. Calcd for [16]aneN_5, $C_{11}H_{27}N_5$: C, 57.60; H, 11.86; N, 30.53. Found: C, 57.25; H, 11.68; N, 30.30. In the case of [17]aneN_5 a viscous oil was obtained, which was not further purified and analyzed. Part of the oil was dissolved in ethanol, and to the ice-cooled solution was added an excess of 37% HCl. The white precipitate of the pentakis(hydrochloride) was recrystallized from aqueous ethanol (slightly acidified with HCl). Anal. Calcd for $C_{12}H_{34}N_5Cl_5$: C, 33.85; H, 8.05; N, 16.45. Found: C, 33.84; H, 7.11; N, 16.30.

Complexes were obtained by mixing with hot equimolar solutions (5×10^{-2}–2×10^{-1} M) of $Ni(ClO_4)_2 \cdot 6H_2O$. After reflux, the blue-violet complexes precipitated. In the reaction with [17]aneN_5, after mixing of reactants, the solution became yellow; the visible spectrum of this solution showed a band at 22.23×10^3 cm^{-1}, which is typical for a tetracoordinate square-planar low-spin complex. It is possible that the first step of complexation of [17]aneN_5 involves coordination by only four atoms; the second step should involve folding of the ligand to coordinate metal with the fifth nitrogen atom. This second step seems to be quite kinetically disfavored. On prolonged reflux (2 days), the violet precipitate of the presumably fully coordinated complex formed. No attempts were made to isolate the yellow intermediate. In all cases, elemental analyses for the three pentaaza macrocyclic complexes corresponded to the formula $Ni(L)(H_2O)(ClO_4)_2$. The complexes were kept under vacuum over concentrated sulfuric acid until completely dehydrated; the dehydrated pentaamine perchlorate complexes were then used for the redox studies in acetonitrile solution.

[Ni([18]aneN_6)](ClO_4)$_2$. [18]aneN_4 is commercially available (Aldrich Europe) as the trisulfate of the hexaammonium ion. To an aqueous solution of this salt was added a stoichiometric amount of $Ba(OH)_2$, and the suspension was refluxed for 1 h. $BaSO_4$ was filtered off, and a hot solution of nickel perchlorate was added. When the mixture was allowed to stand, a violet compound crystallized. The characterization of this complex has been recently reported.[12]

Preparation of the Acetonitrile Solutions of Nickel(III) Macrocyclic Complexes. The CH_3CN solutions of Ni(III) complexes for ESR measurements were in general prepared by chemical oxidation of the

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solutions of the corresponding Ni(II) complexes. To a solution of the Ni(II) complex in anhydrous acetonitrile (distilled consecutively from CaH_2, P_4O_{10}, and CaH_2) was added stoichiometric $NOBF_4$ in a nitrogen atmosphere. Formation of the Ni(III) species was indicated by the appearance of a green color (except for $Ni[12]aneN_4^{3+}$ (orange) and for $Ni[18]aneN_6^{3+}$ (greenish brown)). The solution was transferred with the aid of a syringe, to a quartz tube for ESR measurements, contact with air being carefully avoided; the tube was then kept in liquid nitrogen. In general, the solutions were made 0.1–0.5 M in Bu_4NBF_4, in order to increase resolution of the hyperfine structure of the spectra.[5] In some cases (*sym*- and *asym*-[14]aneN_4 and [15]aneN_5), the Ni(III) complexes, in CH_3CN 0.1 M in Bu_4NBF_4, were obtained through controlled-potential electrolysis using platinum gauzes as the working electrode and counterelectrode and a wire of Ag covered by AgCl as the reference electrode. Solutions obtained by NO^+ oxidation or by electrolysis presented the same ESR spectra.

Electrochemistry. The electrochemical apparatus, cells, and purification of materials have been described elsewhere.[6]

ESR Spectra. X-Band (9 GHz) ESR spectra were recorded with a Varian E-9 ESR Spectrometer equipped with a variable-temperature accessory. The Q-band (35 GHz) spectra were recorded with the same apparatus equipped with a Varian E-111 microwave bridge. The field was calibrated with DPPH ($g = 2.0037$) as a standard.

Visible Spectra. Spectra of the yellow solid $Ni([12]aneN_4)(ClO_4)_2$ and Ni(tren)(ClO_4) complexes were obtained by the filter paper technique using a Beckman DK-2A spectrophotometer. The complexes were ground to give a powder and then spread out on a dried filter paper (Schleicher & Schull, No. 589). Filter paper of the same type was used as a reference. Spectra were recorded in the absorption mode.

Results and Discussion

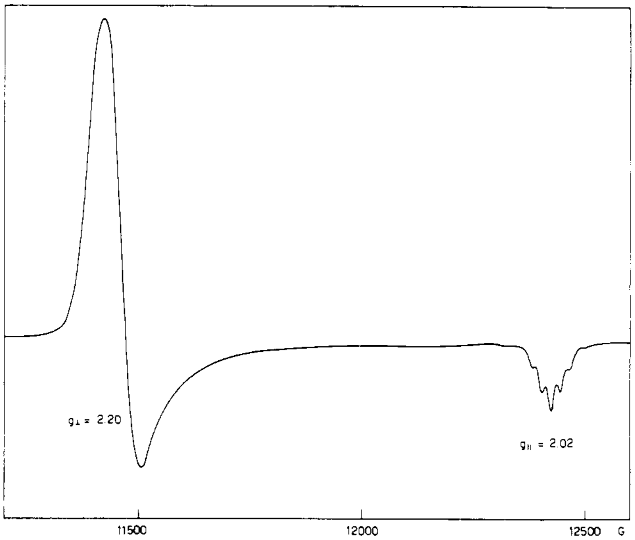

Figure 2. Q-Band (35 GHz) ESR spectrum of $Ni([13]aneN_4)^{3+}$ in acetonitrile solution, 0.1 M in Bu_4NBF_4, frozen at 77 K.

Tetraaza Macrocyclic Complexes. The oxidation behavior in acetonitrile of the nickel(II) complexes with the tetraaza macrocycles **1**–**6** was investigated. The Ni(II) complexes, obtained as perchlorates, are *all* yellow, diamagnetic solids. Color, magnetism, and spectra are those expected for square complexes, in which the ligand is coplanarly chelated (in a more or less distorted fashion). This situation is novel and unexpected for the smallest size macrocycle [12]aneN_4: in fact previously reported solid Ni(II) complexes of [12]aneN_4 were of the high-spin type,[13] in which the ligand was probably folded, in a noncoplanar stereochemistry. The yellow species was obtained in aqueous solution in appreciable concentration at especially high values of temperature and ionic strength (e.g., 6 M $NaClO_4$).[14] We have now found that mixing of hot ethanolic solutions of nickel perchlorate and [12]aneN_4 produced the expected blue precipitate; however, prolonged heating of the ethanolic suspension caused a change to a yellow solid, with an electronic spectrum (on filter paper) typical of a square-planar tetraamine complex. Such a spectrum has a single band in the d–d region with a maximum at 22.47×10^3 cm^{-1}. The corresponding complex with the open-chain analogue of [12]aneN_4, i.e., triethylenetetramine (or 2,2,2-tet), for which a square-planar stereochemistry in the perchlorate complex has been shown by X-ray analysis,[15] exhibits a band maximum at 22.86×10^3 cm^{-1}.[16] When dissolved in acetonitrile, the above complexes do not necessarily maintain their magnetic and stereochemical features but may undergo changes of the coordination number and of the spin state. As a matter of fact, only the complex with [13]aneN_4 remains after dissolution as 100% of the low-spin form. In the case of the complexes with the two 14-membered macrocycles, **3** and **4**, both the square, yellow and the distorted octahedral, blue-violet species coexist in CH_3CN solution, according to the solvent-controlled equilibrium

$$\underset{\text{low spin}}{[\mathrm{NiL}]^{2+}} + 2\mathrm{CH_3CN} \rightleftarrows \underset{\text{high spin}}{[\mathrm{NiL(CH_3CN)_2}]^{2+}}$$

The blue species presumably has a trans-octahedral stereochemistry, as deduced from electronic spectra.[9,17] This type of arrangement has been shown by X-ray analysis in the blue paramagnetic complex [Ni(*sym*-[14]aneN_4)Cl_2].[18] The blue species predominates for both ligands: *sym*-[14]aneN_4, 78%; *asym*-[14]aneN_4, 82%.[6] All the remaining Ni(II) tetraaza macrocyclic complexes exist in acetonitrile solution in the blue-violet high-spin form, as shown by the complete absence of the absorption band of the yellow form (expected at 400–450 nm) in the d–d region. Spectra of these complexes in acetonitrile are those expected for octahedral tetraamine complexes, $[NiL(CH_3CN)_2]^{2+}$. In particular, [15]aneN_4 (**5**) and [16]aneN_4 (**6**) have a cavity size large enough to chelate the high-spin Ni(II) ion in a coplanar fashion, and the formation of trans-octahedral complexes with these ligands has been previously documented.[17] On the other hand, the small aperture of [12]aneN_4 does not allow coplanar coordination, and the $[Ni([12]aneN_4)(CH_3CN)_2]^{2+}$ complex should present a cis-octahedral stereochemistry (ligand folded).

The information about the geometry of the Ni(III) macrocyclic complexes is derived from ESR spectra (at 77 K) of the acetonitrile solutions of the species produced by controlled-potential electrolysis and/or by oxidation with stoichiometric $NOBF_4$. The ESR spectra are those expected for a low-spin d^7 system and can be interpreted with use of an axial $S = {}^1/_2$ spin Hamiltonian. In the case of the complexes with the 13- to 16-membered tetraaza macrocycles, it was found that $g_\perp > g_\parallel \simeq 2.0$. The spectrum of the [13]aneN_4 complex is shown in Figure 2. Similar spectra were previously observed by Busch and associates[5] for other Ni(III) complexes with some neutral saturated or unsaturated quadridentate macro-

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(16) In a recent report (Plassman, W. H.; Swisher, R. G.; Blinn, E. L. *Inorg. Chem.* **1980**, *19*, 1101) it has been claimed that $Ni([12]aneN_4)^{2+}$ in its yellow form should no longer be considered square planar but "five-coordinate" (it was not mentioned explicitly whether square pyramidal or trigonal bipyramidal). The only new experimental findings on which the work is based are the values of $\Delta H°$ and $\Delta S°$ (measured in 6 M $NaClO_4$) for the blue-to-yellow conversion compared with those previously obtained for other macrocyclic complexes (measured in 0.1 M $NaClO_4$). It is well-known that the blue-to-yellow conversion is a solvent-controlled process, and so a large difference in the concentration of the "inert" electrolyte (thus, in the quality of the solvent) makes such a comparison meaningless.

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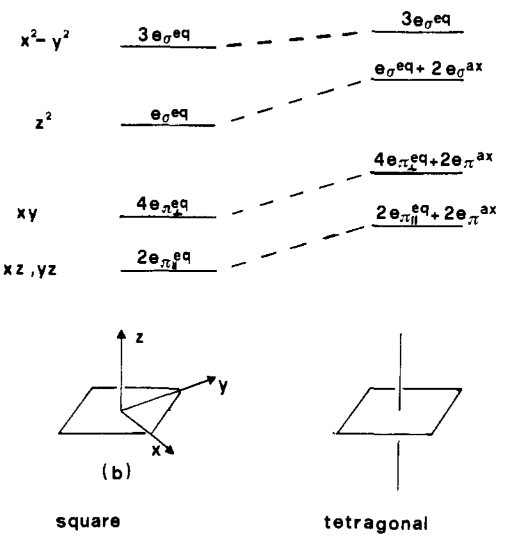


Figure 3. Angular-overlap diagram for square-planar (square) and tetragonally distorted octahedral (tetragonal) stereochemistries.

Table I. Spin-Hamiltonian Parameters of Nickel(III) Complexes with Tetraaza Macrocycles[a]

ligand	$g_\parallel$	$g_\perp$	$A_\parallel$, 10^{-4} cm^{-1}
[12]aneN_4	2.17	2.06	
[13]aneN_4	2.02	2.20	20
sym-[14]aneN_4	2.03	2.20	19
asym-[14]aneN_4	2.03	2.20	19
[15]aneN_4	2.03	2.21	*b*
[16]aneN_4	2.0	2.2	*b*

[a] Calculated from ESR spectra of acetonitrile solutions frozen at 77 K. [b] Poorly resolved $g_\parallel$ feature.

cycles and can be interpreted on the assumption of a tetragonal-octahedral coordination around Ni(III), with the macrocycle occupying the equatorial positions and two solvent molecules in the axial sites. In this situation, the chromophore should have a three-hole $(x^2 - y^2)^2(z^2)^1$ ground-state configuration, as shown in the "tetragonal" scheme of Figure 3, in which the energies of the one-electron levels have been parameterized with use of the angular-overlap model.[19] Furthermore, $g_\parallel$ is split into five lines having an intensity ratio of 1:2:3:2:1, due to the interaction of the unpaired electron with the nuclei of the nitrogen atoms of the CH_3CN molecules in the axial sites. The spin-Hamiltonian parameters of the Ni(III) complexes with the considered tetraaza macrocycles are shown in Table I.

In the case of the Ni(III) complex with the smallest size quadridentate macrocycle, [12]aneN_4, the axial ESR spectrum (reported in Figure 4) shows a reverse order of g values, i.e., $g_\parallel > g_\perp$. This spectrum is indicative of a ground state in which the unpaired electron is located in the xy or $x^2 - y^2$ orbital; in this situation, the ligand field model, at first order,[20] gives

$$g_\parallel = 2.0023 + \frac{8\xi}{\Delta(x^2 - y^2)xy} > g_\perp = 2.0023 + \frac{2\xi}{\Delta xz}$$

where ξ is the one-electron spin-orbit coupling constant and $\Delta(x^2 - y^2)xy$ and Δxz are the energy differences between the states having the unpaired electron in the $(x^2 - y^2)xy$ and xz orbitals and the ground state.

In order to account for this peculiar behavior, one could assume that in the Ni(III) complex the 12-membered macrocycle adopts the tetragonal arrangement previously observed with the other ligands of the series. In the case of a coplanar arrangement of the macrocycle, the presence of an unpaired electron in the xy or $x^2 - y^2$ orbital could be explained if one assumes the following situations:

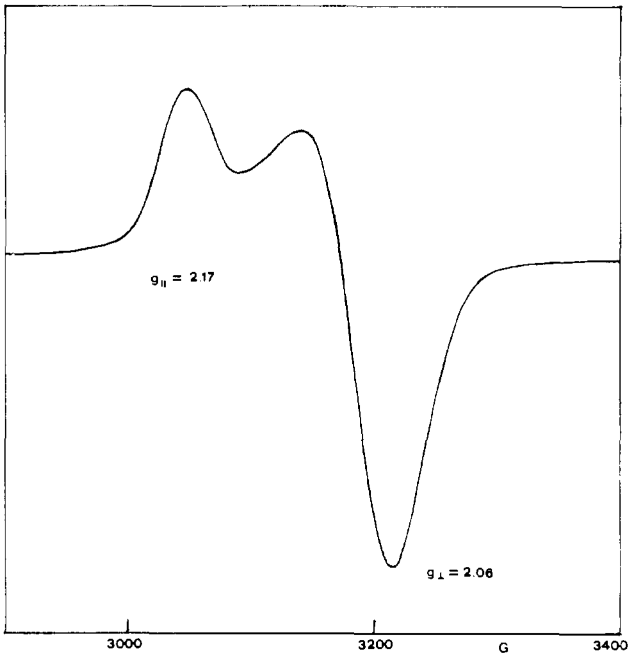
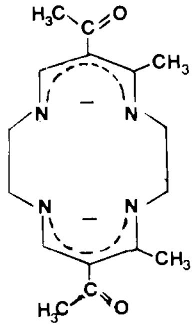


Figure 4. X-Band (9 GHz) ESR spectrum of Ni([12]aneN_4)$^{3+}$ in acetonitrile solution, 0.1 M in Bu_4NBF_4, frozen at 77 K.

(1) The interactions between Ni(III) ion and the axial ligands (CH_3CN) should be stronger than those with the equatorial donor atoms (the amine groups of the macrocycle), i.e., $e_\sigma^{ax} > e_\sigma^{eq}$, so that z^2 should have higher energy than $x^2 - y^2$ (see the "tetragonal" scheme in Figure 3). This situation seems quite unrealistic in view of the lower σ-donor tendency of the nitrogen atom of CH_3CN with respect to the amine nitrogen atom of the macrocycle. On the other hand, a stronger axial σ interaction should occur for a *tetragonally compressed* stereochemical arrangement; this situation also seems improbable, if one considers the small aperture of the 12-membered ligand. Tetragonal compression should eventually occur (but does not) with larger size macrocycles.

(2) A strong π interaction occurs; i.e., $4e_{\pi\perp}^{eq} > e_\sigma^{eq}$ (see the "square" scheme in Figure 3). Thus, the energy of the xy level becomes higher than that of z^2. As a matter of fact, this situation has been observed with Ni(III) complexes with dianionic macrocycles of type I (Jager's macrocycles),[5] in which π electrons are delocalized over the ligand framework. However, an analogous π-donor ability is precluded from the fully saturated neutral tetraamine macrocycle [12]aneN_4.



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It is therefore evident that the ligand's coplanar arrangement found with Ni(III) complexes with larger size macrocycles cannot explain the ESR spectrum of the [Ni([12]aneN_4)]$^{3+}$ complex: the smallest macrocycle must be folded, as it is in

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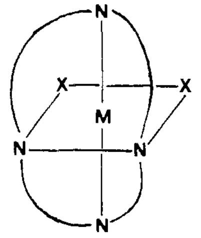
the Ni(II) d^8 high-spin complex. In this connection, it is useful to consider that a folded-ligand configuration has been found in the X-ray-investigated complex $[Co([12]aneN_4)(NO_2)_2]^+$ (the two nitro groups occupying the remaining positions of the polyhedron).[21] Also in view of the close similarity of the two low-spin cations Co(III) and Ni(III), an analogous stereochemistry (shown by structure II) can be hypothesized for the Ni(III) complex of $[12]aneN_4$ in acetonitrile solution. Ligand field calculations of the one-electron energy levels, performed according to a method described elsewhere,[22] using the coordinates found in the complex $[Co([12]aneN_4)(NO_2)_2]^+$ through X-ray analysis[21] and considering that the σ-bonding ability of CH_3CN is lower than that of the donor atoms of the macrocycle ($e_\sigma(CH_3CN) < e_\sigma(\text{amine})$), showed that the higher energy state has a 73% z^2 character and, as a consequence, z^2 should have a higher energy than $x^2 - y^2$. Thus, the ground-state configuration of Ni(III) would be essentially $(x^2 - y^2)^1(z^2)^2$, which gives the observed $g_\parallel > g_\perp$ pattern.



II

Pentaaza Macrocyclic Complexes. The three quinquedentate-ligand Ni(II) complexes (of the high-spin type, as shown by the values of the magnetic moment ranging within 3.0–3.1 μ_B), obtained as perchlorates, dissolve in acetonitrile as 2:1 electrolytes and show electronic spectra expected for a distorted octahedral stereochemistry. The quinquedentate ligand is probably folded to occupy four equatorial positions and one apical position, the sixth one being occupied by a solvent molecule. A similar stereochemistry has been proposed for the Ni(II) complexes with the analogous 15-membered pentaaza macrocycle, in which an amine nitrogen atom has been replaced by a pyridine ring (2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene).[23] Moreover, folding of the latter quinquedentate macrocycle to span five coordination sites of an octahedron has been observed through X-ray studies on the Co(III) derivative.[24]

As far as Ni(III) complexes are concerned, the ESR spectra of the frozen acetonitrile solutions show a $g_\perp > g_\parallel$ pattern, as observed with tetraazamacrocyclic complexes. For all the pentaazamacrocyclic complexes $g_\perp = 2.17$ and $g_\parallel = 2.03$. In every case the $g_\parallel$ feature is resolved into five lines with an average separation of 16×10^{-4} cm^{-1}; the intensity ratio is not that expected for the interaction of the unpaired electron with two equivalent nitrogen atoms in the axial positions. However, in the spectrum of $Ni([16]aneN_5)^{3+}$ in methanol (at 77 K; obtained by oxidation with $S_2O_8^{2-}$), the $g_\parallel$ feature is split into three lines of equal intensity and A is 16×10^{-4} cm^{-1}. This is consistent with the interaction of the unpaired electron with the axially coordinated amine nitrogen atom of the folded ligand. The other axial position of the distorted coordination octahedron should be occupied by a solvent (CH_3OH) molecule. This state of affairs may suggest that the hyperfine pattern observed in acetonitrile solution arises from the interaction of the unpaired electron with two nonequivalent nitrogen nuclei (the macrocycle amine group and the CH_3CN molecule) having comparable values of the hyperfine coupling constant.

Table II. Half-Wave Potentials, $E_{1/2}$ (vs. Ag/AgNO$_3$ (0.01 M)), in Acetonitrile Solution 0.1 M in Et_4NBF_4 at 25 °C, for the Redox Change

$$Ni(\text{macrocycle})^{2+} \rightleftarrows Ni(\text{macrocycle})^{3+} + e^-$$

macrocycle	$E_{1/2}$, V[a]	Δ*p*, mV[b]
$[12]aneN_4$	1.082	100
$[13]aneN_4$	0.7–0.9[c]	
sym-$[14]aneN_4$	0.702	70
asym-$[14]aneN_4$	0.838	72
$[15]aneN_4$	1.012	79
$[16]aneN_4$	1.112	140
$[15]aneN_5$	0.737	80
$[16]aneN_5$	0.772	90
$[17]aneN_5$	0.817	110
$[18]aneN_6$	0.905	95

[a] ±0.005 V. [b] Difference between anodic and cathodic peaks in cyclic voltammetry profiles, recorded at 50 mV s^{-1}. [c] Ill-defined voltammetric response.

The Hexaaza Macrocyclic Complex $[Ni([18]aneN_6)]^{2+/3+}$. The Ni(II) complex of $[18]aneN_6$ $NiL(ClO_4)_2$ presents a three-band electronic spectrum typical for an octahedral chromophore, strictly analogous, for instance, to that of $[Ni(en)_3]^{2+}$. Spectra, in aqueous solution [cm^{-1} × 10^3 (ε, M^{-1} cm^{-1})]: $[Ni([18]aneN_6)]^{2+}$ $\nu_1 = 11.98$ (19), $\nu_2 = 18.85$ (11), $\nu_3 = 28.98$ (11); $[Ni(en)_3]^{2+}$ $\nu_1 = 11.36$, $\nu_2 = 18.52$ (7), $\nu_3 = 29.20$ (11). Addition of NH_3 (to make solution 1 M) does not induce any change in the spectrum of the hexaaza macrocyclic compex, suggesting that all the coordination sites of the octahedron are held by the macrocycle. Full octahedral coordination and conformation of the cyclic hexaamine in high-spin Ni(II) and low-spin Co(III) complexes have been recently discussed by Hay and co-workers.[12] The ESR spectrum of the Ni(III) complex, in frozen acetonitrile, is strictly analogous to that reported in Figure 4: $g_\parallel$ (2.16) is higher than $g_\perp$ (2.06). On the basis of the previous considerations, based on the tetragonal scheme of the AO diagram (Figure 3), the most reasonable explanation is the formation of a tetragonally compressed octahedral complex. To our knowledge, this is the first example of such a stereochemistry for Ni(III) derivatives. An analogous stereochemical arrangement has been proposed, on the basis of ESR studies, for some low-spin d^7 Co(II) six-coordinate complexes with nitrogenous chelating ligands.[25]

Electrochemical Studies on the Ni^{II}/Ni^{III} Redox Change. The electrochemical behavior of the polyaza macrocyclic complexes in acetonitrile solution (which was made 0.1 M in Et_4NBF_4) was investigated by voltammetric studies using stationary (microsphere, CV technique) or nonstationary (rotating or vibrating wire) platinum electrodes. All the considered Ni(II) complexes undergo a one-electron redox change. In the cyclic voltammograms the ratio of the anodic and cathodic peaks was unity and the RPE responses were typically S-shaped (with the difference $E_{3/4} - E_{1/4} \simeq 60$ mV). However, none of the investigated processes can be considered rigorously reversible from an electrochemical point of view; the separation of the peaks in CV profiles, Δ*p*, is higher than the theoretically expected value (59 mV), and its magnitude was found to be dependent upon the potential scan rate. Values of Δ*p*, measured at 50 mV s^{-1}, are reported in Table II. In the same table are reported the values of the half-wave potential, $E_{1/2}$, calculated from CV diagrams. These values

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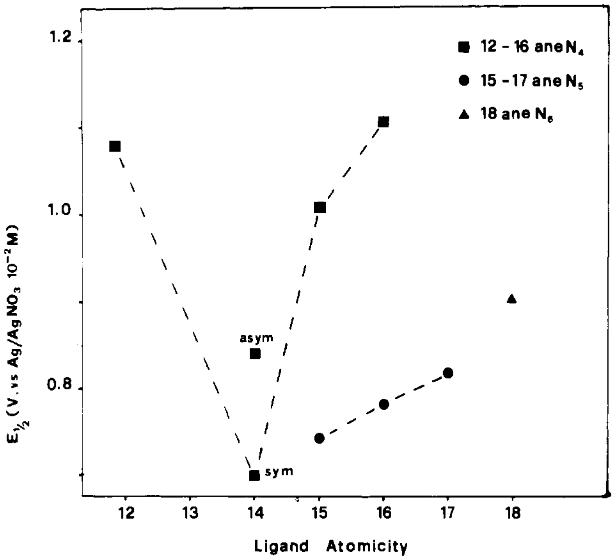

Figure 5. $E_{1/2}$ values for the Ni^{II}/Ni^{III} redox change in complexes with *n*-dentate amine macrocycles ($n = 4, 5, 6$) of increasing cavity size.

are coincident, within the experimental error (±0.005 V), with those obtained from rotating-electrode experiments. The [13]aneN$_4$ complex gives an ill-defined voltammetric response in the 0.7–0.9 V region (vs. Ag/AgNO$_3$ (0.01 M)), and the $E_{1/2}$ value was not evaluated. In spite of this, the Ni(III) complex could be obtained through controlled-potential electrolysis, as well as through chemical oxidation with NO$^+$, as described before.

The half-wave potential, $E_{1/2}$, is a parameter that expresses the relative stability of the +2 and +3 oxidation states. It can be seen in Figure 5, that, for the considered macrocyclic systems, the easiest attainment of the Ni(III) state occurs with the symmetric 14-membered tetraaza ligand (since it has a less positive value of $E_{1/2}$). Among quadridentate systems, structural modifications of the *sym*-[14]aneN$_4$ cavity, which possesses a 5,6,5,6 sequence of the chelate rings, make the access to the Ni(III) state more difficult. In fact (i) rearranging the sequence of the chelate rings, to 5,5,6,6 in the *asym*-[14]aneN$_4$ complex, raises the $E_{1/2}$ values by 140 mV and (ii) progressive expansion of the ligand aperture (15- and 16-membered systems; see Figure 5) causes a progressive increase of the oxidation potential. Correspondingly, a dramatic destabilization of the +3 state is observed when the cavity is contracted to 12 numbers. In other words, the Ni^{II}/Ni^{III} redox process is strongly selective with respect to the ring size, and for the five quadridentate systems investigated, $E_{1/2}$ values span the considerable range of 400 mV.

In quinquedentate systems, the easiest oxidation occurs with the smallest ring ([15]aneN$_2$), and progressive expansion of the macrocyclic cavity produces only a very moderate increase of $E_{1/2}$ (~40 mV/inserted $-CH_2-$, compared to ~150 mV/inserted $-CH_2-$ found in tetraaza systems). Moreover, $E_{1/2}$ values for N$_5$-ligand complexes are more positive only than that of the champion of tetraaza systems, *sym*-[14]aneN$_4$, but are in any case less positive than for all the other N$_4$ systems. Therefore, the introduction of a further nitrogen atom into a N$_4$ framework in general favors the formation of the Ni(III) complex and drastically reduces the ring-size-dependent oxidation selectivity.

Coordination by six nitrogen atoms, linked by ethylenic chains, to produce a presumably sterically constrained coordinative framework, as occurs in the [18]aneN$_6$ complex, disfavors the attainment of the Ni(III) state, with respect to all the quinquedentate and to the 14-membered quadridentate systems, as shown by the more positive value of $E_{1/2}$.

Conclusions

The formation of stable Ni(III) complexes with tetraaza macrocycles is essentially regulated by the ligand ability to establish strong in-plane interactions. The most favorable situation is that of the 14-membered systems, which have the appropriate size to encircle 3d cations and to give strong coordinative bonds. Between the two [14]aneN$_4$ ligands, the symmetric one (known also as *cyclam*) is able to better satisfy the geometrical requirements of the encircled cation (donor atoms at the corners of a square, at the right distances). When the ring deviates from the right size (atomicity larger or smaller than 14), the coordinative array is seriously distorted and the amine atoms exert a lower electron donation toward the metal ion.

Addition of a fifth amine nitrogen atom in an apical position should be expected to favor the formation of the Ni(III) cation, which forms octahedral complexes and which would profit from axial coordination in terms of ligand field stabilization energy. This has not been found in complexes with pentaaza macrocycles. Probably, ligand folding disturbs equatorial coordination, and the advantage coming from the apical coordination is more than compensated by the weakening of the in-plane interactions. In this connection, the disappearance of the ring-size selectivity, which occurs in quinquedentate systems, may arise from a balanced situation, in which the stronger equatorial interactions may correspond to a weaker axial stabilizing effect and vice versa. The existence of a steric constrictive effect is even more evident with the sexidentate cyclic hexaamine: in this case, steric constraints are so large to provoke a rearrangement to the unusual compressed octahedral stereochemistry in the Ni(III) complexes.

Registry No. 7, 295-64-7; 7 pentatosylate, 52601-74-8; **8**, 29783-72-0; **8** pentatosylate, 77320-30-0; **9**, 66802-95-7; **9** pentatosylate, 77320-31-1; **9** pentakis(hydrochloride), 77320-32-2; compound b, 16695-22-0; Ni([12]aneN$_4$)(CH$_3$CN)$_2$$^{3+}$, 77321-17-6; Ni([13]aneN$_4$)(CH$_3$CN)$_2$$^{3+}$, 77321-18-7; Ni(*sym*-[14]aneN$_4$)(CH$_3$CN)$_2$$^{3+}$, 47099-85-4; Ni(*asym*-[14]aneN$_4$)(CH$_3$CN)$_2$$^{3+}$, 77321-19-8; Ni([15]aneN$_4$)(CH$_3$CN)$_2$$^{3+}$, 77321-20-1; Ni([16]aneN$_4$)(CH$_3$CN)$_2$$^{3+}$, 77321-21-2; Ni([15]aneN$_5$)(CH$_3$CN)$^{3+}$, 77321-22-3; Ni([16]aneN$_5$)(CH$_3$CN)$^{3+}$, 77321-23-4; Ni([17]aneN$_5$)(CH$_3$CN)$^{3+}$, 77321-24-5; Ni([18]aneN$_6$)$^{3+}$, 77321-25-6; [Ni([12]aneN$_4$)](ClO$_4$)$_2$, 71911-56-3; [Ni([13]aneN$_4$)](ClO$_4$)$_2$, 71901-50-3; [Ni(*sym*-[14]aneN$_4$)](ClO$_4$)$_2$, 15220-72-1; [Ni(*asym*-[14]aneN$_4$)](ClO$_4$)$_2$, 68344-01-4; [Ni([15]aneN$_4$)](ClO$_4$)$_2$, 71882-19-4; [Ni([16]aneN$_4$)](ClO$_4$)$_2$, 75495-95-3; [Ni([15]aneN$_5$)](ClO$_4$)$_2$, 77321-27-8; [Ni([16]aneN$_5$)](ClO$_4$)$_2$, 77321-29-0; [Ni([17]aneN$_5$)](ClO$_4$)$_2$, 77321-31-4; [Ni([18]aneN$_6$)](ClO$_4$)$_2$, 69057-15-4; 2,2,2-tet tetratosylate disodium salt, 56187-06-5; 2,3,2-tet tetratosylate disodium salt, 77320-33-3; 3,2,3-tet tetratosylate disodium salt, 77320-34-4; 2,2,2-tet, 112-24-3; 2,3,2-tet, 4741-99-5; 3,2,3-tet, 10563-26-5.