

## Trivalent Nickel Bis(triaza macrocyclic) Complexes. Ligand Ring Size and Medium Effects on the Nickel(III)/Nickel(II) Redox Couple Potential

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The formation of nickel(III) bis(triaza macrocyclic) complexes with ligands 1-3 has been investigated in acetonitrile, dimethyl sulfoxide, and water. ESR spectra of frozen acetonitrile solutions of the nickel(III) bis(triaza macrocyclic) complexes are typical of a low-spin  $d^7$  cation and display a rhombic (macrocycles 1 and 2) pattern or axial (3) patterns. Examination of  $E_{1/2}(\text{Ni(II)/Ni(III)})$  values, determined by voltammetric techniques, shows that the easiest attainment of the trivalent state occurs with the smallest size macrocycle 1. In particular, the  $[\text{Ni(1)}_2]^{3+}$  species is formed at an even less positive potential than the  $[\text{Ni(cyclam)}]^{3+}$  complex, considered until now as the most stable Ni(III) species among polyaza macrocyclic complexes. This definitively demonstrates the superiority of six-coordination in stabilizing the Ni(III) oxidation state. The role of the solvent in the formation of trivalent complexes, at the level of both the coordination and the solvation sphere, has been investigated and discussed. Moreover, it has been discovered that, in aqueous solution, the increase of the concentration of the supporting electrolyte ( $\text{NaClO}_4$ ) may disfavor or favor the access to the trivalent state, according to whether water molecules are present or not in the redox equilibrium, thus introducing a novel element of selectivity.

### Introduction

Polyazacycloalkanes represent a unique family of ligands that permit the formation of solution-stable trivalent nickel complexes (through oxidation of the corresponding divalent species), whose stability, expressed by the potential of the Ni(III)/Ni(II) redox couple, may be varied over a substantial range through structural modifications of the macrocyclic framework.<sup>1</sup> The cyclic nature of the ligand imparts kinetic stability to the complex and allows the oxidizing Ni(III) cation to persist in the solution and to be characterized.

We have previously examined the effects of the ligand's denticity and of the ring size on the Ni(III)/Ni(II) redox change in acetonitrile solution for a broad family of tetra-, penta-, and hexaaza fully saturated macrocycles (4-12).<sup>2,3</sup> The results of this study seemed at first paradoxical. In fact it was found that, in contrast to the fact that Ni(III) (in the low-spin state) prefers six-coordination (typically, according to an elongated octahedral arrangement), the easiest access to the trivalent state, expressed by the least positive value of the Ni(III)/Ni(II) redox potential, was found to occur with the quadridentate 14-membered ligand 6, (better known as *cyclam*); on the other hand, the increase of the number of the amine nitrogen atoms to five (9-11) and six (12) unexpectedly involved an increase rather than a decrease of the Ni(III)/Ni(II) redox potential (see Figure 2). We ascribed this to the formation of severe steric constraint in the penta- and hexaaza macrocyclic frameworks, when the ligands fold to span the coordinative sites of the Ni(III) cation. On the contrary, *cyclam* (6) incorporates transition-metal ions in a very relaxed configuration, which permits the formation of especially strong metal-nitrogen interactions:<sup>4</sup> highly charged cations (e.g. Ni(III)) profit from coordination to a larger extent than less charged species (Ni(II)). In particular, the existence of a serious strain in the coordinated hexadentate macrocycle 12 is reflected by the very unusual compressed octahedral stereochemistry that we discovered for the Ni(III) complex.<sup>3</sup>

After that, it was obvious to predict that a ligand or, better, a coordinative system able to exert six-coordination in a strain-free arrangement would definitively favor the achievement of the trivalent nickel state, resulting in a Ni(III)/Ni(II) redox couple potential even less positive than that found for the *cyclam* complex. Wieghardt and co-workers<sup>5</sup> reported the preparation and the characterization of the very stable trivalent nickel bis(triaza

macrocyclic) complex  $[\text{Ni(1)}_2]^{3+}$  (1 = [9]aneN<sub>3</sub>). Indeed, the distribution of the six amine nitrogen atoms in two distinct nine-membered triaza rings may afford full octahedral coordination in a minimum or non-strain situation, and bis(triaza macrocyclic) complexes could be serious candidates to succeed to *cyclam* (6) in the leadership in stabilizing trivalent nickel. The above considerations prompted us to investigate the Ni(II)/Ni(III) change for bis(triaza macrocyclic) species in the classical acetonitrile solution, in order to perform homogeneous comparison of their Ni(III)/Ni(II) redox couple potential values with those of the previously investigated tetra-, penta- and hexaaza ligand complexes. The effect of the ligand ring size was also investigated, considering the 9- to 11-membered triaza macrocycles 1-3.

A further point of interest seemed the effect of the nature of the solvent on the redox change: as a matter of fact, in tetraaza (e.g. *cyclam*) and pentaaza (e.g. [16]aneN<sub>5</sub>) complexes, solvent molecules enter the coordination sphere of the metal, whereas bis(triaza macrocyclic) species, in both the divalent and the trivalent oxidation state, are "coordinatively saturated", and one could expect a substantially different effect on the Ni(III)/Ni(II) redox couple potential when the coordinative tendencies of the solvent are varied. In this connection, a redox investigation has also been performed in dimethyl sulfoxide.

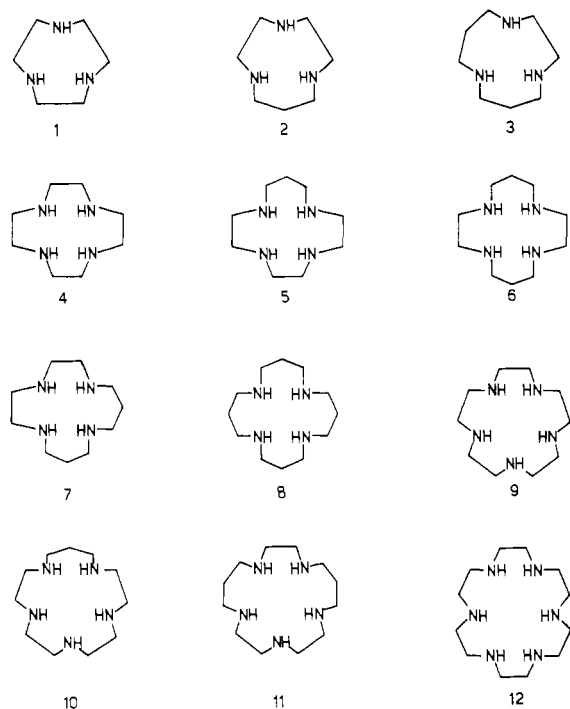
Finally, redox chemistry in water was investigated for representative complexes of tetra- and pentaaza macrocycles and compared to that of the 1:2 complexes of [9]aneN<sub>3</sub>. In this case, it was possible to change in a continuous fashion the solvating properties of the medium, by progressively varying the concentration of the supporting electrolyte ( $\text{NaClO}_4$ ) from 0.1 to 7.0 M. The change in the perchlorate concentration may generate significant stabilizing or destabilizing effects on the Ni(III)/Ni(II) redox couple potential, which are related to the presence of water molecules in the half-reaction equilibrium. This novel effect introduces a further element of selectivity in the old story of the stabilization of trivalent nickel through coordination to polyaza macrocycles of varying denticity and ring size.<sup>6</sup>

### Experimental Section

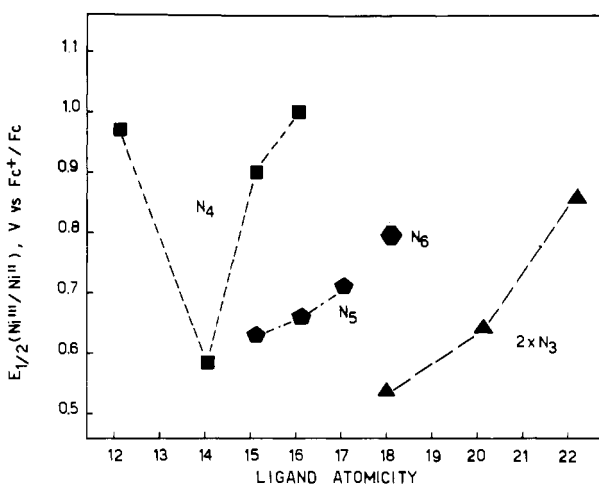
**Synthesis of the Ligands and of Their Nickel Complexes.** Tetra- and pentaaza macrocycles and their nickel complexes were prepared according to published procedures.<sup>3</sup> Triaza macrocycles were prepared by a synthetic route derived from the work of Richman,<sup>10</sup> involving the condensation of appropriate tosylated reagents, according to the following procedures.

- (1) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109-3118.
- (2) Fabbrizzi, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1063-1065.
- (3) Bencini, A.; Fabbrizzi, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544-2549.
- (4) Martin, L. Y.; DeHayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4046-4048.
- (5) Wieghardt, K.; Schmidt, W.; Hermann, W.; Kuppens, H. *J. Inorg. Chem.* **1983**, *22*, 2953-2956.

- (6) Kinetics aspects of the redox reactions of Ni(III) bis(triaza macrocyclic) complexes have been recently considered by McAuley and co-workers.<sup>7-9</sup>
- (7) McAuley, A.; Norman, P. R.; Olobuyide, O. D. *Inorg. Chem.* **1984**, *23*, 1938-1943.
- (8) McAuley, A.; Norman, P. R.; Olobuyide, O. D. *J. Chem. Soc. Dalton Trans.* **1984**, 1501-1505.
- (9) McAuley, A.; Norman, P. R. *Isr. J. Chem.* **1985**, *25*, 106-111.
- (10) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268-2270.



**Figure 1.** Saturated polyaza macrocycles considered in this work. Ligands are also indicated by the general formula  $[X]aneN_y$ , where the number  $X$  indicates the atomicity (number of carbon and nitrogen atoms forming the ring) and  $y$  is the number of the amino groups.

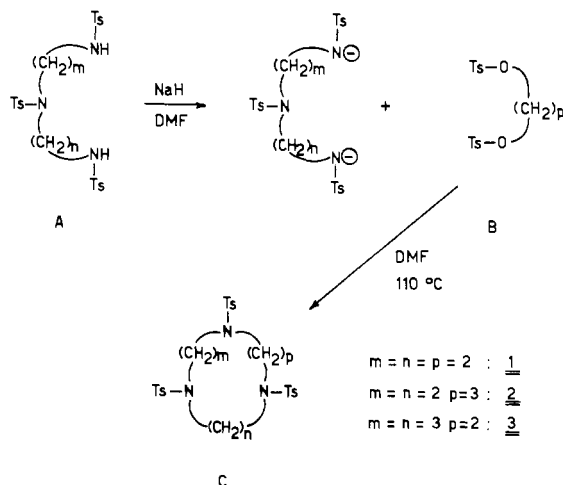


**Figure 2.** Half-wave potential values measured in acetonitrile solution (0.1 M  $Et_4NBF_4$ , 25 °C) for the Ni(III)/Ni(II) redox change for polyaza macrocyclic complexes. Points N4, N5, and N6 refer to 1:1 metal complexes with [12,14–16]ane $N_4$  (4, 6–8), [15–17]ane $N_5$  (9–11), and [18]ane $N_6$  (12) macrocycles respectively. 2 x N3 points refer to the 1:2 metal complexes with [9–11]ane $N_3$  (1–3) ligands (see Results and Discussion).

(i) **Tosylated Triamine (A).** In a typical preparation, the amine (diethylenetriamine or dipropylenetriamine—0.16 mol) was dissolved in 160 mL of water containing NaOH (0.5 mol) in a 2-L round-bottomed flask. Under vigorous stirring, 100 g of *p*-toluenesulfonyl chloride, dissolved in 500 mL of diethyl ether, was added to the aqueous solution over 3 to 4 h; when the addition was complete, stirring was continued overnight. The white precipitate was filtered off, washed with water and methanol, and dried under vacuum. The dried solid was suspended in ethanol (200 mL) and warmed for 30 min. A crystalline white solid was obtained, which was dried under vacuum for 2–3 days. The yield varied between 60 and 80%.

(ii) **Tosylated Diol (B).** A 100-g sample of *p*-toluenesulfonyl chloride dissolved in 500 mL of ether was added under vigorous stirring to 0.25 mol of the diol (1,2-ethanediol or 1,3-propanediol) dissolved in 160 mL of triethylamine in a 2-L round-bottomed flask over 3 to 4 h; at the end of the addition the mixture was stirred overnight. The white solid was filtered off, washed with water and ethanol, and dried under vacuum.

### Scheme I



The dried solid was suspended in ethanol and warmed for 30 min. The microcrystalline product was dried in vacuo for 2–3 days; the yield varied between 60 and 80%.

**Cyclization.** A 0.1-mol sample of the tosylated triamine (A) was dissolved in anhydrous DMF (1.1 L, freshly distilled from  $CaH_2$ ) in a nitrogen atmosphere. To the well-stirred solution was added a large excess of NaH (0.6 mol, oil suspension) in portions, and the mixture was stirred until effervescence subsided and then heated at 70 °C for about 3 h. The solution was then allowed to cool and filtered under nitrogen, to remove unreacted NaH, into a 2-L round-bottomed flask, previously flushed with nitrogen. To this solution, heated at 105 °C, was added 0.1 mol of B in 400 mL of anhydrous DMF under nitrogen over 2–3 h. Heating and stirring were continued overnight. The yellow solution was then allowed to cool and concentrated at reduced pressure to 250 mL; the concentrate was added, with efficient stirring, to 3–4 L of water and left to precipitate overnight. The precipitate was collected by filtration, washed with water, ethanol, and ether, and dried under vacuum. The crude product was recrystallized from  $CHCl_3/EtOH$ , giving a whitish solid; yield 50 to 60%.

**Hydrolysis of the Tritosylated Macrocycle.** A 0.04-mol sample of the tritosylate (C) was dissolved in 70 mL of 96% sulfuric acid, and the mixture was kept at 105 °C for 96 h. The mixture was cooled in an ice bath, and 170 mL of ethanol was cautiously added, followed by 400 mL of ether. A gray-brown solid separated, which was treated with decolorizing charcoal in water (120 mL). The brown solution thus obtained was concentrated on a rotary evaporator to 20 mL; to this solution was added 50 mL of 10 M NaOH, and a little  $Na_2SO_4$  precipitated, which was removed by filtration. The solution was extracted with 5 x 50-mL portions of chloroform, and the extracts were dried over sodium sulfate overnight. The solvent was removed in a stream of nitrogen, giving an oily residue, which was dissolved in 20 mL of ethanol. To this solution, cooled in an ice–water bath, was added a large excess of concentrated aqueous HCl, giving a white solid, which was collected by filtration under nitrogen, washed with ethanol and ether, and dried under vacuum.

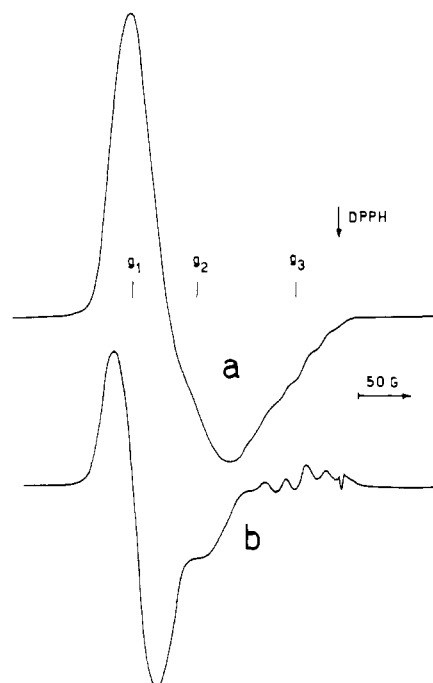
**[9]ane $N_3$ ·3HCl.** Anal. Calcd for  $C_6H_{18}N_3Cl_3$ : C, 30.2; H, 7.6; N, 17.6. Found: C, 30.02; H, 7.50; N, 17.31.  $^{13}C$  NMR: 41.3 ppm. Mp 284–285 °C dec.

**[10]ane $N_3$ ·3HCl.** Anal. Calcd for  $C_7H_{20}N_3Cl_3$ : C, 33.28; H, 7.98; N, 16.63. Found: C, 33.01; H, 8.1; N, 16.51.  $^{13}C$  NMR: 20.5, 42.82, 44.37 ppm. Mp: 245–246 °C dec.

**[11]ane $N_3$ ·3HCl.** Anal. Calcd for  $C_8H_{22}N_3Cl_3$ : C, 36.04; H, 8.31; N, 15.76. Found: C, 36.02; H, 8.58; N, 15.51.  $^{13}C$  NMR: 19.75, 42.04, 43.86 ppm. Mp: 240–241 °C dec.

Bis(triamine)nickel(II) complexes were prepared by dissolving the cyclic ligand trihydrochloride (0.002 mol) in water/ethanol 1:1, followed by the addition of aqueous NaOH (0.006 mol) and ethanolic  $Ni(ClO_4)_2$  (0.0008 mol). The reaction mixture became violet upon adding the Ni(II) solution and was refluxed for 30 min and then allowed to cool to room temperature. The violet crystalline precipitate that formed was collected by filtration, washed with ethanol and ether, and dried under vacuum. All the complexes gave satisfactory elemental analyses.

**Electrochemistry.** The experiments were performed on an AMEL Electrochemolab system. Cyclic voltammetry experiments were performed by using a three-electrode cell. For measurements in aqueous solutions, the working electrode was a carbon-paste electrode and the reference electrode (SCE) was separated from the cell, which contained aqueous  $NaClO_4$  as supporting electrolyte, by a bridge fitted with a ceramic frit and filled with saturated NaCl solution to avoid precipitation



**Figure 3.** ESR spectra of a frozen (77 K) acetonitrile solution of the  $[\text{Ni}([\text{9}] \text{aneN}_3)_2]^{3+}$  complex: (a) first derivative; (b) second derivative.

of  $\text{KClO}_4$ . For nonaqueous solution studies a platinum microsphere was used as a working electrode. A silver wire was employed as a pseudo reference electrode, which was calibrated with respect to the  $(\text{Fc}^+/\text{Fc})$  redox couple. In particular, an equimolar amount of ferrocene was added to the  $10^{-3}$  M solution of the nickel(II) macrocycle complex and the  $E_{1/2}(\text{Ni}(\text{III})/\text{Ni}(\text{II}))$  was obtained from the peak "distance" from ferrocene. In nonaqueous solutions,  $\text{Et}_4\text{NBF}_4$  (Erba, Polarographic Grade) was used as supporting electrolyte. MeCN was refluxed over  $\text{CaH}_2$  and then distilled and stored under nitrogen over molecular sieves.  $\text{Me}_2\text{SO}$  dried over  $\text{CaH}_2$  was distilled under reduced pressure and stored under nitrogen. Solvent vapor saturated nitrogen was used to deaerate the solutions and to maintain an inert atmosphere in the cell, which was kept at  $25.0 \pm 0.1$  °C.

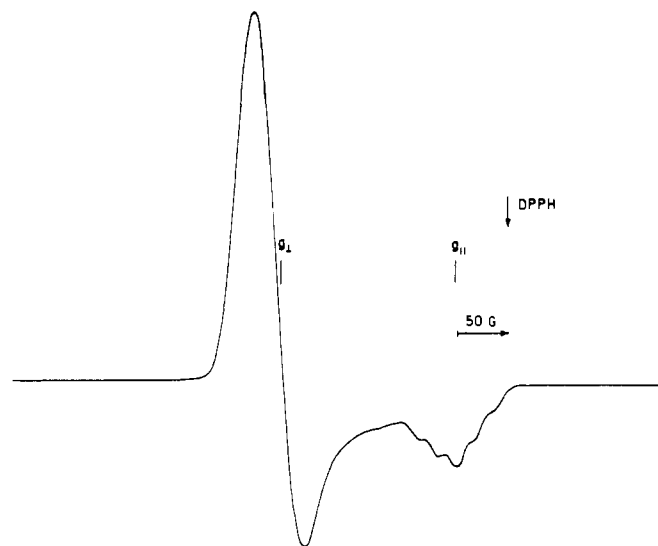
Controlled potential electrolysis experiments were performed with platinum gauze as a working electrode. The working electrode and the counter electrode compartments were connected through a U-shaped bridge.

**ESR Measurements.** ESR spectra were measured at 77 K on magnetically diluted glasses in acetonitrile, by using a Varian E-109 X-band spectrometer;  $g$  values were determined relative to DPPH.

## Results and Discussion

**Stereochemistry of the Ni(III)/Ni(II) Redox Change.** The stereochemistry of the high-spin nickel(II) bis(triaza macrocyclic) complexes (ligands **1**–**3**) is well-defined on the basis of X-ray diffraction and spectral investigations. The crystal structure of the  $[\text{Ni}([\text{9}] \text{aneN}_3)_2](\text{NO}_3)\text{Cl}$  complex salt has been reported,<sup>11</sup> showing octahedral hexacoordination, with a small trigonal distortion. The Ni(II)(high-spin)–N distance ranges in the  $2.10 \pm 0.01$  Å interval. Similarity of the d–d spectra suggest analogous stereochemical arrangements also for the  $[\text{Ni}([\text{10}] \text{aneN}_3)_2]^{2+}$  and  $[\text{Ni}([\text{11}] \text{aneN}_3)_2]^{2+}$  chromophores.<sup>12</sup>

In this work, green solutions (in acetonitrile) of the nickel(III) triaza macrocyclic complexes have been obtained through controlled-potential electrolysis and/or through chemical oxidation with excess  $\text{NOBF}_4$  of the violet Ni(II) corresponding species. Direct pieces of information on the stereochemistry and spin state of the oxidized macrocyclic complexes were obtained from the ESR spectra of their frozen (at 77 K) solutions. The spectra (Figures 3 and 4) are those for a  $d^7$  low-spin cation, unambiguously demonstrating the authenticity of the Ni(III) state. In particular, Figure 3 reports the spectrum of  $[\text{Ni}(\mathbf{1})_2]^{3+}$  complex (part a), which shows a three- $g$  pattern, indicative of a rhombic stereo-



**Figure 4.** ESR (first derivative) spectrum of a frozen (77 K) acetonitrile solution of the  $[\text{Ni}([\text{11}] \text{aneN}_3)_2]^{3+}$  complex.

chemistry. The rhombic nature of the ESR signal is definitively evident from the second-derivative spectrum in the lower part of the figure (part b). ESR parameters are  $g_1 = 2.14$ ,  $g_2 = 2.09$ ,  $g_3 = 2.03$ , and  $A_3 = 19$  G.<sup>13</sup>  $[\text{Ni}(\mathbf{2})_2]^{3+}$  also displays a totally analogous rhombic pattern ( $g_1 = 2.14$ ,  $g_2 = 2.09$ ,  $g_3 = 2.03$ ,  $A_3 = 17$  G). On the other hand, the  $[\text{Ni}(\mathbf{3})_2]^{3+}$  complex shows a typically axial spectrum (Figure 4;  $g_{\perp} = 2.15$ ,  $g_{\parallel} = 2.03$ ,  $A_{\parallel} = 18$  G). The parallel portion of the spectrum is split into five lines indicating the presence of two equivalent nitrogen atoms in the apical sites. This latter spectrum is qualitatively similar to those found for nickel(III) tetraaza macrocyclic complexes (e.g.  $[\text{Ni}[\text{13}] \text{aneN}_4]^{3+}$ ),<sup>3</sup> where apical positions were occupied by nitrogen atoms of the MeCN molecules. The difference of the ESR response, rhombic for  $[\text{Ni}(\mathbf{1})_2]^{3+}$  and  $[\text{Ni}(\mathbf{2})_2]^{3+}$  and axial for  $[\text{Ni}(\mathbf{3})_2]^{3+}$ , can be ascribed to the different structural properties of the considered triaza macrocycles. In the case of the more flexible 11-membered ring (**3**), for each triaza moiety, two nitrogen atoms, probably those linked by the ethylenic chain, coordinate in the equatorial plane, whereas the remaining nitrogen atom, bound by the more flexible propylenic arms, occupies the apical position of the elongated octahedron.<sup>14</sup> On the contrary, the Ni(III) complexes with the smaller ring size macrocycles **1** and **2** exhibit a less symmetric rhombic arrangement, deviating from the typical elongated octahedral stereochemistry generally observed with tetra- and pentaamine macrocyclic complexes. However, pieces of information on the solution stability of the above Ni(III) complexes (relatively to the corresponding Ni(II) species) can only be obtained from redox potential values (vide infra).

X-ray data on nickel(III) bis(triaza macrocyclic) complexes are not yet available. However, the crystal structure has been reported for the Ni(III) complex with the ligand 1,4,7-triazacyclononane- $N,N,N'$ -triacetate, in which three acetate arms are bound to the **1** framework through the nitrogen atoms.<sup>16</sup> The complex presents a roughly octahedral stereochemistry: the

(13) The room-temperature spectrum shows a broad singlet with a  $g$  value of 2.09, indicating that also under these conditions the oxidized species is an authentic Ni(III) complex.

(14) The large inertness toward decomplexation of nickel(II) bis(triaza macrocyclic) complexes<sup>15</sup> rules out the possibility that MeCN molecules displace macrocyclic nitrogen atoms and occupy axial positions, thus being responsible for the splitting in five lines of the  $g_{\parallel}$  feature. ESR spectra of the  $[\text{Ni}^{\text{III}}([\text{11}] \text{aneN}_3)_2]^{3+}$  complex in non-nitrogen donor solvents (e.g.  $\text{Me}_2\text{SO}$ ) could not be recorded due to the very limited persistence in solution of the trivalent species. However, it is worth to notice that for the more kinetically stable  $[\text{Ni}^{\text{III}}([\text{9}] \text{aneN}_3)_2]^{3+}$  complex in frozen aqueous solution the  $g_{\perp}$  feature is distinctly split into five lines, clearly indicating apical amine nitrogen coordination.

(15) Murphy, L. J.; Zompa, L. J. *Inorg. Chem.* **1979**, *18*, 3278–3281.

(16) van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489–3490.

(11) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157–L159.  
(12) Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531–2536.

Ni(III)-N distances are appreciably different, being 1.91, 1.93, and 1.94 Å.

**Ni(III)/Ni(II) Redox Couple Potentials in MeCN.** Due to its excellent resistance to oxidation, acetonitrile has been widely used for the study of the formation of metal complexes in unusually high oxidation states. In particular, the broadest collection of electrochemical data for polyaza macrocyclic Ni(II) and Ni(III) complexes refers to MeCN solutions.<sup>1-3,17-21</sup>

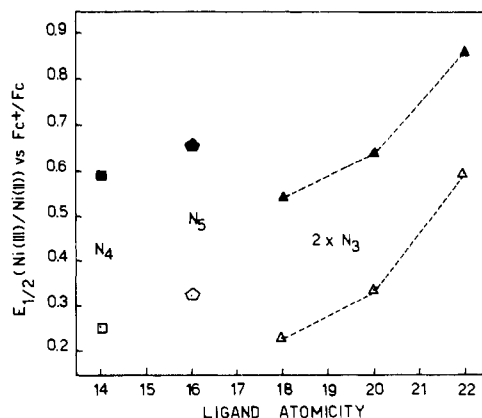
On cyclic voltammetry investigation, nickel(II) bis(triaza macrocyclic) complexes of 1-3 display a quasi-reversible one-electron-oxidation process, the ratio of the anodic and cathodic peaks being equal to unity in the explored potential scan rate range (20-200 mV/s). Peak separation is in any case larger than theoretically expected for a fully reversible process ((1) 75, (2) 125, (3), and 115 mV at 100 mV/s potential scan rate). The half-wave potential values, measured vs. the internal reference couple  $Fc^+/Fc$ , are reported in Figure 2, with those referring to quadri-, quinque-, and sexidentate amine macrocycles. For comparative purposes, we assign to bis(triaza macrocyclic) complexes an atomicity number that is the sum of the atomicity values of each ring (see Figure 2).

There are several points worthy of interest.

(i) The size of the triaza macrocyclic ring affects the formation of the trivalent complex: in particular, the easiest access to the Ni(III) state occurs with the smallest ring 1 and progressive expansion of the ligand cavity makes the formation of the oxidized complex more difficult (see Figure 2). A similar type of selectivity had been found with complexes of quinquedentate macrocycles 9-11.<sup>2,3</sup> A possible explanation lies in the different size of divalent and trivalent nickel cations. First, as inferred from the values of the Ni-N distances available from X-ray data, the Ni(II) (high-spin) to Ni(III) (low-spin) redox change in octahedral environments involves a drastic contraction of the metal radius (about 10%) and the smallest size triaza macrocycle is expected to be better arranged for coordination at a shorter distance. Second, when the metal ion dimensions are decreased, the two triaza moieties must approach closer to each other and nonbonding repulsive interactions become more and more important with the increasing length of the aliphatic chain of the macrocycle. In this connection it should be recalled that, in the case of the 12-membered macrocycle [12]aneN<sub>3</sub>, inter-ligand repulsions are strong enough to hinder the formation of the 1:2 complex.<sup>12</sup> It should also be noted that, in the case of quadridentate ligands, ring size selectivity displays a completely different pattern and small variations of the macrocyclic aperture cause dramatic effects on the relative stability of the Ni(III) complexes.<sup>3,18</sup> This would mean that Ni(II) and Ni(III) cations are much more sensitive to changes of the intensity of the in-plane (*xy*) interactions (tetraaza macrocyclic complexes) than of those experienced in an octahedral environment (pentaaza and bis(triaza macrocyclic) complexes).

(ii) The formally 18-membered, hexacoordinated [Ni(1)<sub>2</sub>]<sup>3+</sup> complex is formed at a remarkably less positive potential (250 mV) than the corresponding complex with the 18-membered sexidentate macrocycle 12. Comparison is homogeneous in the sense that in both systems six secondary amine nitrogen atoms are bound to nickel. The very large difference of the Ni(III) relative stability emphasizes the severe steric constraints experienced by the hexaaza macrocycle during the Ni(II)/Ni(III) oxidation process (and concomitant ion size contraction). "Cutting" the sexidentate macrocycle into two triaza moieties removes most of the steric strains and permits a very easy attainment of the trivalent nickel state.

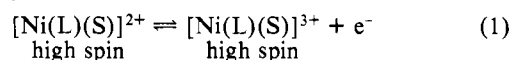
(iii) The formation of the [Ni(1)<sub>2</sub>]<sup>3+</sup> complex occurs at a less positive potential than for the [Ni(cyclam)]<sup>3+</sup> species, reported until now as the most favorable situation to obtain trivalent nickel



**Figure 5.** Half-wave potential values for the Ni(III)/Ni(II) redox change in MeCN (full symbols) and Me<sub>2</sub>SO (open symbols) (0.1 M in Et<sub>4</sub>NBF<sub>4</sub>). Systems investigated were 1:1 complexes with [14]aneN<sub>4</sub> (squares) and [16]aneN<sub>5</sub> (pentagons) and 1:2 complexes with [9-11]aneN<sub>3</sub> macrocycles (triangles).

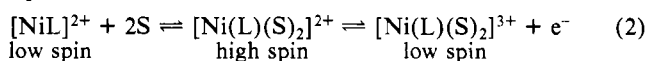
for amine donors. This definitively demonstrates the superiority of six-coordination over in-plane four-coordination, in the absence of serious steric constraints. The advantage of bis(triaza) coordination to Ni(III) compared to that of cyclam and its enhancement will be further considered in the next paragraphs.

**Solvent Effects on the Stabilization of Nickel(III) Polyaza Macrocyclic Complexes.** Acetonitrile, even if the most popular, is not the only solvent (other than water) that allows one to handle nickel(III) polyaza macrocyclic complexes. Dimethyl sulfoxide (Me<sub>2</sub>SO) is also an excellent solvent for the same job. Cyclic voltammetry investigations on the Ni(III)/Ni(II) redox change for some selected polyaza systems have been performed in Me<sub>2</sub>SO solution, and the corresponding  $E_{1/2}$  values are compared with those obtained in MeCN solution (see Figure 5). For both solvents,  $E_{1/2}$  values have been measured with respect to the internal reference redox couple  $Fc^+/Fc$ . Thus, relying on the usual assumption that the  $Fc^+/Fc$  redox couple potential is independent of the solvent, comparison of the data obtained in MeCN and in Me<sub>2</sub>SO should permit one to directly evaluate the role of the medium on the formation of the Ni(III) complexes. Let us first consider, for simplicity sake, the complexes of the quinquedentate ligand [16]aneN<sub>5</sub> (10). For this system the redox change can be represented by



One solvent molecule (S) participates in the coordination sphere of both Ni(II) and Ni(III) complexes, occupying a site of the octahedron. This solvent molecule is believed to bind more strongly to the trivalent cation than to the divalent one. Therefore, the fact that Me<sub>2</sub>SO stabilizes Ni(III) to a larger extent than MeCN ( $E_{1/2}$  value less positive by 350 mV) should be ascribed to the greater coordinating tendencies of the former solvent. This behavior is consistent with the general acid-base Gutmann scale, according to which Me<sub>2</sub>SO has much greater donor number than MeCN (29.8 and 14.1 respectively).<sup>22</sup>

In the case of cyclam complexes, an analogous behavior has been observed. The situation, in this case, is complicated by the fact that the Ni(II) complex undergoes the high-spin/low spin equilibrium



and the distribution of the two Ni(II) species is different with the two systems (for MeCN, high spin = 81%, low spin = 19%; for Me<sub>2</sub>SO, high spin = 30%, low spin = 70%). The fact that two solvent molecules are involved and that, in the case of the more coordinating Me<sub>2</sub>SO solvent, there is a predominance of the low-spin planar species would infer a greater stabilizing effect of

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Me<sub>2</sub>SO. On the contrary, the MeCN–Me<sub>2</sub>SO potential difference is almost the same as that found with the [16]aneN<sub>5</sub> system.

Even more surprising is the behavior of the three investigated bis(triaza macrocyclic) complexes (see Figure 5). In contrast with the fact that the complexes are coordinatively saturated and there is no room for the solvent in the coordination sphere, a sharp solvent effect is observed, which is of the same order as that found for the previously considered coordinatively unsaturated macrocyclic complexes.

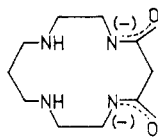
This unexpected state of affairs suggests that the stabilization of highly charged cations by a solvent may also occur through second-sphere solute–solvent interactions and, in particular, that solvation plays as an important role as coordination. It may be possible that due to solvation effects the Fc<sup>+</sup>/Fc redox couple potential is not strictly the same in solvents of different solvating properties; thus, an absolute comparison of redox potential values vs. Fc<sup>+</sup>/Fc obtained in different media may be not correct. However, it is significant that, for the systems investigated in this work, changing the solvent produces almost the same effect, independent of the fact that the solvent molecules are included or not in the coordination sphere of the redox active species, unambiguously indicating that the solvent can display its “coordinating” tendencies both through direct coordination (first sphere) or solvation (second sphere), and the two modes of interaction deserve equal attention.

**Ni(III)/Ni(II) Redox Change in Aqueous Solution. Effect of the Variation of the Concentration of the Supporting Electrolyte (NaClO<sub>4</sub>, 0.1–7.0 M).** The Ni(III)/Ni(II) redox change for the above macrocyclic complexes has also been investigated in aqueous solution. Whereas [Ni(1)<sub>2</sub>]<sup>2+/3+</sup> and [Ni(2)<sub>2</sub>]<sup>2+/3+</sup> systems disclose reversible CV profiles on a carbon-paste working electrode, the [Ni(3)<sub>2</sub>]<sup>2+</sup> complex displays a totally irreversible behavior, the trivalent species being unstable even on the time scale of the cyclic voltammetry experiment performed at conventional potential scan rates (20–200 mV/s). The trend of *E*<sub>1/2</sub> values for reversible systems parallels the one found in nonaqueous solutions (0.1 M NaClO<sub>4</sub>: [Ni(1)<sub>2</sub>]<sup>2+/3+</sup>, 0.711 V vs. SCE; [Ni(2)<sub>2</sub>]<sup>2+/3+</sup>, 0.770 V; [Ni(6)]<sup>2+/3+</sup>, 0.74 V; [Ni(11)]<sup>2+/3+</sup>, 0.795 V). Sodium perchlorate was employed as supporting electrolyte due to its very reduced coordinating tendencies toward metal ions.

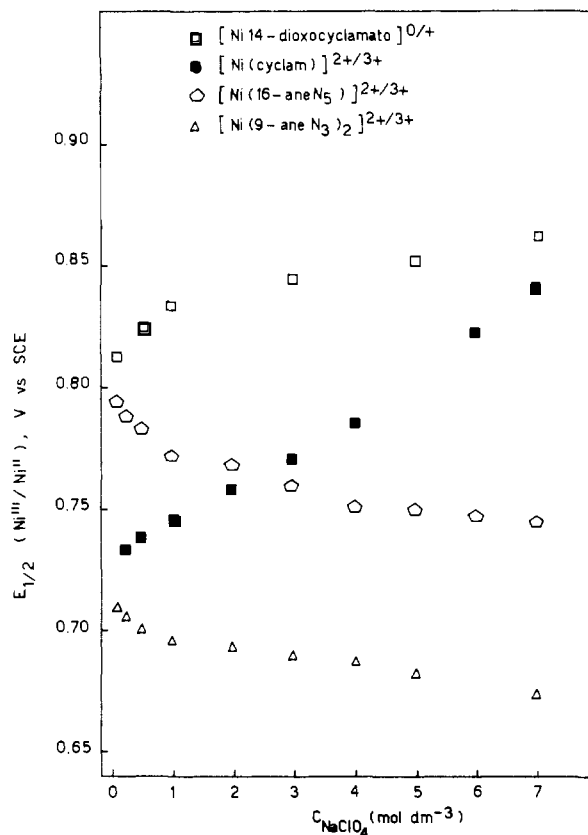
We have recently discovered that the variation of the concentration of the supporting electrolyte (NaClO<sub>4</sub>) may selectively affect the thermodynamic stability of M(II) and M(III) (M = Ni, Cu) complexes with dioxocyclamato ligands, substantially modifying the value of the M(III)/M(II) redox couple potential:<sup>23</sup> in particular, the increase of NaClO<sub>4</sub> concentration (from 0.1 to 7.0 M) favors the formation of Cu(III) and disfavors the formation of Ni(III).

We have now been interested in looking at a possible effect of NaClO<sub>4</sub> on the oxidation behavior of polyaza macrocyclic Ni(II) complexes, coordinatively saturated or not. In particular, we have measured the *E*<sub>1/2</sub> (Ni(III)/Ni(II)) for [Ni([9]aneN<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and for complexes of some representative polyaza macrocycles: the quadridentate **6** (cyclam) and the quinquedentate **10** ([16]aneN<sub>5</sub>), in aqueous solutions containing increasing amounts of the “inert electrolyte” (NaClO<sub>4</sub>). The corresponding values are displayed in Figure 6; the trend of *E*<sub>1/2</sub>(Ni(III)/Ni(II)) is not the same for all the investigated complexes: with some ligands the formation of the trivalent complex is favored by the increasing NaClO<sub>4</sub> concentration; with other ligands the opposite occurs.

For comparative purposes, data for the [Ni(14-dioxocyclamato)]<sup>0/+</sup> ([Ni(13)]<sup>0/+</sup>) have been reported. For this

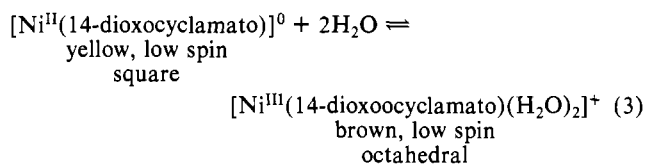


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**Figure 6.** Half-wave potential values for the Ni(III)/Ni(II) redox change in polyaza macrocyclic complexes measured in aqueous solutions at varying concentrations of the supporting electrolyte (0.1–7.0 M NaClO<sub>4</sub>).

complex the increase of the inert salt concentration causes a progressive increase of the *E*<sub>1/2</sub>(Ni(III)/Ni(II)) values, indicating a progressively more difficult attainment of the trivalent state. The oxidation process may be represented as



The supporting electrolyte competes for water molecules with the Ni(II) species and, by subtracting them from the left side of eq 3, displaces to the left the oxidation equilibrium.

A similar trend is observed with the cyclam complex, and an analogous explanation could be proposed. In this case, the Ni(II) species, in contrast to what is found for the 14-dioxocyclamato complex, exists as 71% of square species and 29% of the octahedral.<sup>24</sup> However, an increase in NaClO<sub>4</sub> concentration favors the yellow square species, which, at NaClO<sub>4</sub> concentrations equal to or higher than 3 M, is present as 100%. Moreover, the cyclam system (for which a 2+/3+ charge variation occurs in the oxidation process) appears to be more sensitive to the variation of the supporting electrolyte concentration than the dioxocyclam system (0/+1 charge variation).

On the contrary, for the [16]aneN<sub>5</sub> (**10**), and ([9]aneN<sub>3</sub>)<sub>2</sub> (**1**) complexes, the increase of the NaClO<sub>4</sub> concentration causes a decrease of the Ni(III)/Ni(II) redox couple potential, i.e. favors the formation of the trivalent species. It is to be noted that in both redox equilibria water does not appear as a reactant (in the pentaaza macrocyclic complex, a water molecule being coordinated both to the divalent and the trivalent species) and the competing effect of the inert electrolyte is not expected. The fact that, rather than insensitivity to NaClO<sub>4</sub>, a stabilizing effect is observed could

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be ascribed to the stabilization experienced by an highly charged cation (Ni(III)) in an environment of increasing negative charge (due to the increase of  $\text{ClO}_4^-$  ions).

On increasing the  $\text{NaClO}_4$  concentration, because of the opposite effects described above, the difference in stability of the Ni(III) complexes with [9]ane $\text{N}_3$  and cyclam, expressed by  $\Delta E_{1/2}$ , which is quite small at low  $\text{NaClO}_4$  concentrations (0.1 M  $\text{NaClO}_4$ ,  $\Delta E_{1/2} = 25$  mV), becomes larger and larger (7 M, 160 mV). Moreover for  $\text{NaClO}_4$  concentrations greater than 3 M (see Figure 6), the  $E_{1/2}(\text{Ni(III)}/\text{Ni(II)})$  value for the [16]ane $\text{N}_3$  complex becomes less positive than that of the cyclam analogue, thus inverting the previously established, apparently well-defined order.

### Conclusions

This work has tried to throw light into the factors that control

the attainment of the trivalent state of nickel polyamine complexes in solution. At this stage, the following conclusions can be drawn.

(1) The structural properties of the ligand (in particular the ring size) are a very selective element in the stabilization of Ni(III); this is particularly evident in the case of quadridentate macrocycles.

(2) Changing the solvent does not alter the relative trend of stability of Ni(III) complexes with different macrocycles: the nature of the solvent is not selective.

(3) In aqueous solutions the variation of the concentration of the so-called "inert" electrolyte introduces a novel element of selectivity, discriminating between redox changes involving or not involving water molecules.

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## Reactions of $\text{MoS}_3$ , $\text{WS}_3$ , $\text{WSe}_3$ , and $\text{NbSe}_3$ with Lithium. Metal Cluster Rearrangement Revealed by EXAFS

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EXAFS analysis has been used to study the structural changes that occur during the lithiation of the amorphous materials  $\text{MoS}_3$ ,  $\text{WS}_3$ , and  $\text{WSe}_3$  and the crystalline material  $\text{NbSe}_3$ . For the three amorphous materials, an increase in the number of metal-metal bonds was observed, as well as a significant decrease in the metal-metal distance. A reduction in the number of metal-chalcogenide interactions was also apparent, along with an increase in the metal-chalcogenide distance. For  $\text{Li}_4\text{MoS}_3$ , the predicted Mo-Mo and Mo-S distances are 2.66 (3) and 2.50 (3) Å, respectively. A reasonable model for this fully lithiated structure involves an octahedral  $\text{Mo}_6$  cluster analogous to those found in Chevrel-phase materials. Similar clusters may be formed during lithiation of  $\text{WS}_3$  and  $\text{WSe}_3$ . Predicted W-W and W-S distances were 2.64 (3) and 2.47 (3) Å for  $\text{Li}_4\text{WS}_3$ ; for  $\text{Li}_5\text{WSe}_3$ , W-W and W-Se distances of 2.67 (3) and 2.61 (3) Å were found. In contrast with that of the amorphous trichalcogenides, lithiation of crystalline  $\text{NbSe}_3$  results in a slight contraction of the average Nb-Se bond length. From Se EXAFS, it was found that a significant Se-Se interaction persists in this material after lithiation, and it is difficult to say whether or not significant metal cluster formation occurs. These results have implications for interpretation of the electrochemical behavior of these materials.

### Introduction

The chemistry of molybdenum and tungsten combined with sulfur and selenium is extremely rich in its structural diversity and practical importance. The dichalcogenides ( $\text{ME}_2$ ; M = Mo, W; E = S, Se) are well understood structurally, and are important for their catalytic and electrochemical properties.<sup>2</sup> The trichalcogenides ( $\text{ME}_3$ ) are amorphous materials, which have been shown to react readily with *n*-butyllithium and alkali-metal naphthalides to form amorphous compositions such as  $\text{M}'_x\text{MoS}_3$  ( $\text{M}' = \text{Li, Na, K}$ ;  $0 \leq x \leq 4$ ).<sup>3</sup> Electrochemically,  $\text{MoS}_3$  cathodes in lithium cells show good reversibility provided they are not discharged further than the composition  $\text{Li}_3\text{MoS}_3$ .<sup>4</sup> The amorphous structure of these materials,<sup>5</sup> whether prepared by thermal or solution techniques,<sup>6</sup> has hindered their characterization. The Chevrel phases  $\text{M}'_x\text{Mo}_6\text{E}_8$  form a third class of molybdenum chalcogenides. These systems have been extensively studied because of their superconducting properties. Formally, the molybdenum oxidation state varies from +2 to  $+2\frac{2}{3}$  depending on the value of *x*, overlapping that observed in the most reduced of the amorphous trichalcogenide compositions.

In a previous paper, EXAFS results on the untreated  $\text{ME}_3$  materials were described.<sup>7</sup> Despite their lack of long-range order, local structure involving metal-metal bonding was observed, and a chainlike structure for  $\text{MoS}_3$  was proposed.<sup>8</sup> This paper describes the dramatic structural changes that occur upon electro-

chemical lithiation of these materials. Clear evidence is found for the formation of higher order metal clusters, and a hexanuclear octahedral model is proposed for  $\text{Li}_4\text{MoS}_3$ . It thus appears that the amorphous trichalcogenides are important intermediates that can be transformed to dichalcogenides by heat or the Chevrel phase analogues electrochemically.

### Experimental Section

**Sample Preparation and Data Collection.** The  $\text{ME}_3$  starting materials were prepared by previously described methods from the  $(\text{NH}_4)_2\text{ME}_4$  precursors.<sup>7</sup> Lithium was inserted into the trichalcogenides at ambient temperature either by electrochemical means or by reaction with *n*-butyllithium in dry hexane using published procedures.<sup>3</sup> Open-circuit voltages for 15  $\text{Li}_x\text{MoS}_3$  samples prepared by reaction with *n*-butyllithium were measured for comparison with the previous electrochemical

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