N-(Aminoethyl)cyclam: A Tetraaza Macrocyle with a Coordinating Tail (Scorpiand). Acidity Controlled Coordination of the Side Chain to Nickel(II) and Nickel(III) Cations

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Abstract: The novel functionalized macrocycle N-(aminoethyl)cyclam (4, L), in which a NH2CH2CH2- chain is appended to a tetraaza ring, has been prepared through a convenient route, whose key step involves the reaction of tritosylated cyclam and tosylaziridine. The nickel(II) ion is incorporated by the rigid basal tetraaza ring to give a species particularly resistant to demetalation, whereas the coordination by the amine group of the flexible side chain is controlled by the acidity. At pH >2.8 the [NiIII]L3+ species predominates, in which the side arm is apically bound (blue, high-spin complex); at pH <2.8 the predominant form is [NiIIIL]2+, in which the amine group of the side chain is protonated and which is a mixture of a blue high-spin form and of a yellow low-spin form. The nickel(II) complexes undergo a reversible one-electron oxidation process to give an authentic nickel(III) species in which the axial binding of the side arm is again controlled by the acidity. However, in this case the protonation of the side arm is sluggish, which allows the very unusual simultaneous voltammetric characterization of the [NiIII]L3+ and the [NiIIIIL]4+ species. Comparison of the redox potential values with those of reference tetraaza macrocyclic systems demonstrates a stabilization effect on the NiIII state, due to the apical binding by the primary amine group of the side chain.

Tetraaza macrocycles carrying a pendant side chain which contains an additional, potentially coordinating, nitrogen atom represent a novel class of quinquedentate ligands for transition-metal ions which couple two distinct properties: (i) the tendency of the rigid tetraaza ring to incorporate the metal (e.g., NiII, CuII) giving a kinetically stable species, specially resistant to demetalation; and (ii) the capability of the flexible pendant arm to further coordinate the metal ion in one of the axial positions of the octahedron, according to a labile binding mode.

The first example of ligands of this type has been described by Kaden,1 who prepared molecule 1 through metal template condensation of 2,6-diacetylpyridine with a diethylenetriamine moiety carrying the side chain, followed by hydrogenation of the imine bonds and demetalation in boiling cyanide solution. More recent approaches involved the N-substitution on the selectively protected isocyclam ring, followed by deprotection in concentrated sulfuric acid,2 or the nontemplate condensation of tosylated polyamine fragments3 (molecules of type 2 and 3).

In the metal complexes with the above ligands, special attention has been paid to the effects of the coordination of the pendant arm on the properties of the cation incorporated by the basal ring. In particular, in the case of the nickel(II) complex of 1, it has been observed that the species in which the side chain is coordinated is high spin (blue color), whereas the species with the uncoordinated side arm is low spin (yellow).4

The behavior in aqueous solution is spectacular since the neutral blue solution turns yellow on addition of strong acid, due to the competition of hydrogen ions for the amine group of the pendant arm. In this sense this nickel(II) complex behaves as an acid-base indicator, with a distinct pKa value, its color changing back and forth from violet to yellow through consecutive additions of H+ and OH- ions.

In view of the active role of the tail, which can further “bite” an already chelated metal ion, and following the current trend to give ligands picturesque names recalling things of real life, one could suggest naming the above class of molecules scorpiands.

A further, potentially very interesting aspect of the chemistry of metal scorpionate complexes, which has not yet been explored, is the modification of the redox activity of the encircled metal ion through the side arm coordination. As a matter of fact, it is well-known that incorporation of a 3d metal ion by a macrocyclic polyamine ring permits the access to unusually high and otherwise unstable oxidation states, due to a combined effect of kinetic and thermodynamic stabilization.5 Of special interest is the case of the trivalent nickel cation. In fact, whereas the NiIII, d7 low-spin cation prefers six-coordination, according to a distorted octahedral stereochemistry,6 the easiest access to the NiIII state occurs with the quadridentate 14-membered macrocycle cyclam, rather than with ligands of greater denticity, i.e., penta- or hexaaza rings:7 this apparent paradox has been explained considering the very special tendency of cyclam to exert a particularly strong in-plane field, a property precluded to quinque- and sexidentate macro-

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cycles, in which severe steric constraints arise when the ligand folds around the metal ion. The above arguments may suggest that a scorpionoid molecule having the cyclam ring could facilitate oxidation to the Ni^{II} state due to the combined effects of a strong in-plane ligand field and the coordination by a fifth amine group in one of the axial sites of the distorted octahedron. Furthermore, the basal cyclam ring should impart the greatest kinetic stability and resistance to the extrusion of the metal, compared to tetraaza rings of the same or different atomicity.

The above considerations prompted us to develop the new scorpionoid 4 in which a -CH_{2}CH_{2}NH_{2} arm has been added on a nitrogen atom of the privileged cyclam ring: a primary amine group, rather than a secondary or tertiary one, has been chosen due to its greater coordinating tendency and to minimize steric repulsion effects. This work reports the convenient synthesis of 4 (N-(aminoethyl)cyclam) and the solution behavior of its nickel(II) complex, with a special regard to the oxidation process to the trivalent state in nonaqueous and aqueous solvents. In the latter medium we have discovered a singular kinetic effect in the competition of H^{+} and Ni^{III} ions for the side chain amine group.

Experimental Section

Synthesis of 4. The synthetic route to the scorpionoid 4 is outlined in Scheme 1.

The preparation of the key intermediates N,N',N''-tritosylcyclam (6) and tosylaziridine (7) has been described. To a refluxing solution of 6 in MeCN (8 g, 0.012 mol in 300 mL), in a three-neck, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel, was added dropwise a solution of 7 in MeCN (3.5 g, 0.018 mol in 120 mL). The course of the reaction was followed through TLC tests on silica (Stratocrom SI, Carlo Erba, Milan) with a CHCl_{3}/n-hexane/CH_{3}OH mixture (8:4:1) as eluent. After 48 h of refluxing, the spot corresponding to 6 (R_{f} 0.35) had disappeared and only the spot of product 8 (R_{f} 0.7) was present. The reaction mixture was allowed to cool and rotary evaporated to a white powder which was purified by column chromatography on silica (Silica Gel 60, Fluka) using 8:4:1 CHCl_{3}/n-hexane/CH_{3}OH mixture (8:4:1) as eluent. After 48 h of standing, the white microcrystalline solid (5.6 g, 54%). Calcd for C_{40}H_{53}N_{5}S_{4}O_{8}: C, 28.76; H, 5.83; N, 13.97. Found: C, 28.47; H, 5.83; N, 13.97.

Feature: Perchlorate salts of metal complexes are explosive and due care must be employed when handling them. In particular, such compounds should never be heated as solids.

Solution Chemistry Studies. UV-visible absorption spectra were measured on a Cary 2300 spectrophotometer (Varian) with use of 1 cm quartz cells. In the study of the pH dependent behavior of the nickel(II) scorpionoid complex, a 5 \times 10^{-4} M solution of Ni(4)(ClO_{4})_{2}, made acidic with HClO_{4}, was titrated with standard NaOH solution, the pH being measured with a glass electrode. At selected pH values, 3-mL samples of the solution were transferred from the potentiometric cell to a quartz cuvette to record the absorption spectrum and then transferred back to the titration vessel. The pH value was found not to be affected by the above operation.

ESR spectra of the Ni^{III} complexes were recorded on a Varian E-109 spectrometer; g values were calibrated vs. DPPH. The solutions of the Ni^{III} complex were obtained through controlled potential electrolysis with use of a platinum gauze as anode (Me_{2}SO solution) or by chemical oxidation (NOBF_{4} in Me_{2}SO; Na_{2}S_{2}O_{8} in aqueous HClO_{4} solutions) and then transferred to the quartz ESR tube and frozen at the liquid nitrogen temperature.

Voltammetry studies were performed in three-electrode cell connected to either an AMEL (Milan, Italy) Model 563 (CV and AC measurements) or an AMEL 472 electrochemistry apparatus (DPV measurements). Voltammograms were recorded on a Hewlett-Packard 7040A X-Y recorder. For studies in Me_{2}SO solution the working electrode was a platinum microsphere and the pseudoferrocyanide electrode was a silver wire calibrated vs. the Fe^{3+}/Fe^{2+} reference couple. In aqueous solution studies a carbon paste electrode was used as the working electrode and a saturated calomel electrode, connected to the cell through a salt bridge filled with NaCl solution, was used as the reference electrode.

In both spectrophotometric and voltammetric studies the temperature of the solution (25 °C) was controlled by circulating thermostated water.

Results and Discussion

1. Design of the Ligand. Synthesis of the scorpionoid 4 is based on the reaction of Ts-cyclam, 5, a cyclam ring having all but one protected amine groups, with the electrophilic moiety tosylaziridine 7 (see Scheme 1). The synthesis is particularly convenient due
Figure 2. Absorption spectra of a $9 \times 10^{-3}$ M solution of Ni(4)(ClO$_4$)$_2$, made 0.1 M in NaClO$_4$, measured at varying pH values: (1) 2.00; (2) 2.20; (3) 2.30; (4) 2.45; (5) 2.65; (6) 2.80; (7) 3.00; (8) 3.20; (9) 3.40; (10) 3.60; (11) 3.60; (12) 4.20. At higher pH values (up to pH 12) the spectrum did not show further changes. The dotted line refers to a solution made 0.1 M in HClO$_4$, in which the complex should exist as 100% of the [Ni$^{III}$LH]$^{2+}$ form.

Figure 3. Molar Absorptivity plots (10$^{-1}$ cm$^{-1}$ mol) for the bands of the "octahedral" high-spin chromophore (at 508 and 350 nm) are present and that below pH 4 a band at 464 nm begins to appear. This band, typical of a low-spin Ni$^{II}$ tetramine complex, becomes more intense with decreasing pH, whereas the intensity of the bands centered at 508 and 350 nm simultaneously decreases.

If an aqueous solution of [Ni(4)](ClO$_4$)$_2$, containing an excess of strong acid, is titrated with standard base, the pH vs. moles of NaOH plot displays the profile expected for a weak acid (NiLH$^+$), for which a pK$_a$ value of 2.8 can be calculated (K$_a$ = 1/K$^+$, K$_a$ being the constant of equilibrium 1).

It is useful to consider the pK$_a$ value as being made up by two distinct contributions, according to eq 2

$$pK_a = pK_a(-NH_3) - \log K(Ni^{II} + -NH_3)$$

pK$_a(-NH_3)$ refers to the process in which the side arm $-NH_3^+$ group is deprotonated, whereas log $K(Ni^{II} + -NH_3)$ refers to the apical coordination of the $-NH_3$ group to the macrocycle-encircled metal.

One could guess that the pK$_a(-NH_3)$ value is not too distant from the pK$_a$ value of ethylenediamine: 6.8 (assuming that the basal amine group bound to the Ni$^{III}$$^+$ exerts the same repulsive effect of a $-NH_2$ group). On this basis a value of 4 log units is calculated for log $K(Ni^{II} + -NH_3)$. This value is much greater than that observed for the addition of a fifth ammonia molecule to Ni$^{II}$, log K$_a$ = 0.8. However, it should be considered that the coordination of the side arm $-NH_3$ group is favored, compared to that of the NH$_3$ molecule, by the chelate effect. Chelate effect contributions of 3 log units are typically observed in the solution chemistry of metal–amine complexes.

Moreover, a closer inspection of Figure 2 may indicate that the simple equation 1 is not adequate to justify the pH dependence of the visible absorption spectrum of the Ni$^{II}$-scorpionate complex. As a matter of fact, (i) at pH 2.8, where 50% of the nickel complex is present as the [NiLH]$^{2+}$ species, the measured value of the molar extinction coefficient, $\epsilon$, of the band at 464 nm is 23 mol$^{-1}$ L cm$^{-1}$, a value much lower than the halve of the limiting $\epsilon$ value for low-spin nickel(II) tetraaza macrocyclic complexes (typically ranging from 70 to 100 mol$^{-1}$ L cm$^{-1}$). (ii) and in 0.1 M HClO$_4$, where the nickel(II) scorpionate complex should exist as 100% of the protonated form, [NiL(H)]$^{2+}$, the $\epsilon$ value at 464 nm (45 L mol$^{-1}$ cm$^{-1}$) is still very low. Moreover, the band at 350 nm of the high-spin nickel(II) complex is still present. This state of affairs can be explained by admitting that the protonated species [NiLH]$^{2+}$ exists as an equilibrium mixture of the blue, high-spin complex and of the yellow, low-spin species, a situation that is typical for nickel(II) complexes with 14-membered tetraaza macrocycles. The above hypothesis is confirmed by the following evidence: (i) further additions of inert electrolyte to the acidic solution (0.1 M HClO$_4$) of the scorpionate complex make the intensity of the band at 464 nm increase; (ii) a further increase is observed if the solution is heated. It is well-known that the blue-to-yellow interconversion equilibrium involving Ni$^{II}$-tetramine complexes is displaced to the right by an increase of both ionic strength and temperature. Thus, the pH induced color change
observed in solution of the scorpiate complex here investigated should be better interpreted on the basis of the equilibria depicted in Scheme II.

In the definitely acidic conditions (pH < 2.8) we perceive the solution as yellow due to the much greater extinction coefficient of the low-spin species compared to the high-spin one.

3. The NiII/NiIII Redox Change in Nonaqueous Solution. A further aspect of the solution chemistry of nickel(II) scorpiate complexes that deserves special attention is the investigation of the NiII/NiIII oxidation process and the evaluation of any stabilization effect on the NiIII state due to the side chain coordination. First, the NiII/NiIII redox change has been studied in a nonaqueous medium. Dimethyl sulfoxide has been chosen for the following reasons: as an aprotic medium it will not induce any complication of the redox equilibria due to the protonation of the amine group of the pendant arm; moreover, the oxygen coordinating fragment does not cause any hyperfine splitting of the ESR signals of the NiIII complex and does not compete with the ligand's nitrogen atoms (I = 1).

The [Ni(4)]2+ complex in Me2SO solution undergoes a reversible one-electron oxidation process, as shown by cyclic voltammetry experiments at a platinum microsphere. The one-electron stoichiometry has been confirmed through coulometric measurements performed during controlled potential electrolysis with a platinum gauze as working electrode. During the experiment, the blue–violet solution of the NiII in the working electrode compartment turns green, the typical color of trivalent nickel polyamine complexes.

The UV–vis spectrum of the blue NiII solution presents the typical bands of the high-spin complex ($g_s = 5.30$ nm, $e = 10.8$ L mol$^{-1}$ cm$^{-1}$; $g_{\perp} = 3.40$, $e = 21.9$). No band is observed at 450–470 nm, where the absorption of the yellow chromophore is expected. Furthermore, increasing the temperature up to 60 °C does not cause any change of the spectrum. The above findings are consistent with a pseudooctahedral stereochemistry of the high-spin NiII complex, in which the axial sites are occupied by the amine group of the pendant arm and by a solvent molecule. On the other hand, pieces of information on the electronic and stereochemical properties of the NiIII complexes are given by the ESR experiment.

As a matter of fact, the ESR spectrum of the frozen green solution obtained through controlled potential electrolysis or by oxidation with NOBF$_4$ (see Figure 3) presents an axial symmetry with $g_{\perp}$ considerably greater than $g_s$. This is consistent with the formation of an authentic NiIII complex, $d^3$ low-spin. Moreover, the $g_s$ feature is split into three lines of equal intensity, as expected for coordination by a nitrogen atom (that of the pendant arm) in one of the axial positions. Therefore, the redox change in Me$_2$SO seems to occur according to an uncomplicated mechanism involving species of similar stereochemistry (the distorted octahedron) in which the scorpion exerts full coordination, as shown in eq 3.

\[
[Ni^{III}(\text{solvent})]^2+ = [Ni^{III}(\text{solvent})]^3+ + e^- \quad d^3, \text{high spin} \quad d^2, \text{low spin}
\]
The value for $E_{1/2}$ given pH value. Through the weighted combination of eq to the relative concentrations of $[\text{Ni}^{1}\text{IL}^{2+}$ and $[\text{Ni}^{1}\text{IL}^{3+}$ at a side chain is axially coordinated.

whose $E_{1/2}$ value should vary with the hydrogen ion concentration in the AC or DPV profiles) is obtained, whose solution (see Figure 3) and is indicative of the presence, in the investigated pH zone, of only one trivalent species, in which the side chain is axially coordinated.

Thus, two redox active divalent species are present: $[\text{Ni}^{2}\text{L}]^{2+}$, which is oxidized to the trivalent form through the half-reaction I in Scheme III, whose formal potential is $E^{*}_{1/2}$ and $[\text{Ni}^{2}\text{IL}^{3+}$, which is oxidized to the trivalent form through the half-reaction II, whose formal potential is $E^{*}_{1/2}$. As a consequence, each of the two half-reactions I and II should originate an individual wave, whose $E_{1/2}$ value should vary with the hydrogen ion concentration according to the following equations

$$E_{1/2}(I) = E^{*}_{1} + 0.05916 \log (1 + K_{H}[H^{+}]) \quad (4)$$

$$E_{1/2}(II) = E^{*}_{II} + 0.05916 \log ([H^{+}] + K_{H}^{-1}) \quad (5)$$

Since the protonation/deprotonation equilibrium involving the side arm in divalent complexes is fast compared to the time scale of the voltammetry experiment, a single wave (e.g., a single peak in the AC or DPV profiles) is obtained, whose $E_{1/2}$ value results from the contributions of $E_{1/2}(I)$ and $E_{1/2}(II)$, weighted according to the relative concentrations of $[\text{Ni}^{2}\text{L}]^{2+}$ and $[\text{Ni}^{2}\text{IL}^{3+}$ at a given pH value. Through the weighted combination of eq 4 and 5, the following general equation is obtained

$$E_{1/2} = \frac{1}{1 + K[H^{+}]} \frac{E^{*}_{1} + 0.05916 \log (1 + K_{H}[H^{+}])}{1 + K[H^{+}]} + \frac{K[H^{+}]}{1 + K[H^{+}]} \frac{E^{*}_{II} + 0.05916 \log (K_{H}^{-1} + [H^{+}])}{1 + K[H^{+}]} \quad (6)$$

To $E^{*}_{1}$ is ascribed the value of $E_{1/2}$ measured in neutral solution. The value for $E^{*}_{II}$ is calculated from eq 5, using the $E_{1/2}$ value measured at the lowest pH ([H$^{+}$] = $10^{-2}$ M). Now, it can be seen in the $E_{1/2}$ vs $p$H diagram in Figure 4 that the general eq 6 (represented by the solid line) fits quite well the measured $E_{1/2}$ values. Thus, independence of $E_{1/2}$ upon pH is explained on the basis of balanced contributions of two mutually related pH dependent redox equilibria.

At concentrations of strong acid greater than $10^{-2}$ M, due to the variation of junction potentials, the acidity effects on the redox behavior cannot be expressed in terms of pH. Thus, voltammetry profiles (Figure 6) refer to solutions of varying analytical concentration of HClO$_4$. At moderate acidity levels (C(HClO$_4$) = $1 \times 10^{-2}$ M) only one peak is observed. However, on increasing the acidity, the intensity of this peak decreases and a new peak at a potential 200 mV more positive begins to form. In particular, at C(HClO$_4$) = 6 $\times 10^{-2}$ M the two peaks exhibit the same intensity. Finally, at C(HClO$_4$) = 2 $\times 10^{-1}$ M the first peak has disappeared and the second peak has reached its limiting value.

Pieces of information about the stereochemical nature of the oxidized scorpionate complexes can be obtained from the ESR experiments (see Figure 5). The ESR spectrum of the solution of C(HClO$_4$) = $10^{-2}$ M, for which only the first peak is present in the voltammetry profile (spectrum a in Figure 5), corresponds to the previously described $[\text{Ni}^{2}\text{L}]^{2+}$ species, in which the side arm is axially bound to the metal. On the other hand, in definitely acidic conditions, C(HClO$_4$) = 2 $\times 10^{-1}$ M and more, for which only the second, higher potential peak is observed, a totally different spectrum (b in Figure 5) is obtained, still exhibiting axial symmetry, but displaying g values substantially different than those of spectrum a and close to those observed for $[\text{Ni}^{2}\text{L}^{2+}$] in the same conditions. Moreover, the g feature appears as a single

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Figure 5. ESR spectrum of aqueous frozen solutions (77 K) of Ni(4)$^{2+}$ at varying concentrations of HClO$_4$: (a) C(HClO$_4$) = 0.01 M, the signal is due to the $[\text{Ni}^{2}\text{L}]^{2+}$ species, $g_{1} = 2.16, g_{2} = 2.03$; (b) C(HClO$_4$) = 0.2 M, the signal is due to the $[\text{Ni}^{2}\text{IL}^{3+}$ species, $g_{1} = 2.23, g_{2} = 2.02$; compare to $[\text{Ni}^{2}\text{L}^{2+}$] in the same conditions. The g feature appears as a single

![Figure 5](image-url)

Figure 6. Alternating current voltammetry profiles (oxidation scan) obtained for aqueous solutions of Ni(4)ClO$_4$ of varying concentrations of HClO$_4$: (1) C(HClO$_4$) = $1 \times 10^{-2}$ M; (2) $3 \times 10^{-2}$ M; (3) $6 \times 10^{-2}$ M; (4) $1 \times 10^{-1}$ M; (5) $2 \times 10^{-1}$ M.

Scheme IV

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Ni$^{2+}$L$^{2+}$ - H$^{+}$

K$^{+}$

Ni$^{2+}$L$^{3+}$ - H$^{+}$

$E_{1/2}(I)$

$E^{*}_{1} + 0.05916 \log (1 + K_{H}[H^{+}])$

$E_{1/2}(II)$

$E^{*}_{II} + 0.05916 \log ([H^{+}] + K_{H}^{-1})$
line. The above findings are consistent with the formation of the
[NIII(LH)]** species, in which the pendant arm is protonated and
both apical positions are occupied by water molecules. Thus, the
one-electron oxidation process involving the [NI(4)]** complex
at pH < 2 can be described by Scheme IV.

The fact that two waves are observed in the oxidation scan
indicates that equilibrium c, which involves the protonation/de-
protonation of the side arm in the trivalent complex, is slow
compared to the time scale of the voltammetric investigation.
Thus, the employed technique is able to simultaneously detect
the two distinct redox events and does not give the weighted single
response as observed for solutions of lower acidity as previously
described. The result is singular and surprising and the inter-
pretation does not seem straightforward. In fact, there is no
previous experimental evidence nor theoretical support for sluggish
substitution reactions at the axial sites of the d7 cations. However,
it is possible that the abstraction of one electron from the metal
center of the [NIII(LH)]** complex induces, through changes of the
metal–nitrogen bond distances, a rearrangement of the
macroyclic backbone, which makes sterically difficult the binding
of the side chains to one of the axial sites. Further investigations
on the acidity dependence of the solution behavior of NiIII and NiIII
complexes with scorpiands of varying structural features may help
to throw light on this novel and singular aspect of the redox
chemistry of macrocyclic complexes.

5. Electrostatic Influence of the Protonated Side Chain on the
NiII/NiIII Oxidation Process. In Table I are reported the E1/2
values associated with the NiII/NiIII oxidation process for the complexes of 4 and related polyaza macrocycles, measured in 1 M HClO4 aqueous solution. Comparison to the reference Me-
cyclam system shows a behavior opposite to that observed in Me2SO solution: the access to the trivalent state in the Me-cyclam
complex is favored by 140 mV compared to the scorpiand complex. However, it should be considered that in the present conditions the redox equilibrium for the scorpiand system is represented by

\[
\text{[NIII(LH)]}^{2+} \rightleftharpoons \text{[NIII(LH)]}^{4+} + e^- \quad (7)
\]

Thus, any favorable axial coordination effect (observed in
Me2SO solution) is excluded. Moreover, the process of the increase of the charge of the metal center from 2+ to 3+ is made more
difficult due to the presence of a positive charge (of the ammonium
group of the side chain) at a distance of 5.31 Å (as calculated by
molecular models).18

Finally, we have observed a singular phenomenon that may
be related to the presence of a positively charged group (–NH3+) at a relatively short distance from the metal center. We have
described in subsection 2 that addition of NaClO4 to an acidic
e.g., 0.1 M HClO4 solution of Ni(4)(ClO4)2 causes the intensity
of the band of the yellow planar species to increase. However,
if made strongly saline (C(NaClO4) ≥ 3 M), the solution turns
an intense yellow–green color and the typical smell of chlorine
develops. The color is due to a strong absorption band at 290 nm
(with a shoulder at 360 nm), which is typical for NiIII–tetraine complexes,19 which is observed in the Ni(4)** complex generated
through chemical oxidation of a diluted solution ([ClO4] = 0.1 M).
As judged from the molar extinction coefficient at 290 nm, only part of the NiIII complex is oxidized to NiIII and the concen-
tration of the trivalent complex increases when the concentra-
tion of NaClO4 is increased. Noticeably, the intense yellow–
green color (and the chlorine smell) also develops when solid
Ni(4)(ClO4)2 is dissolved in an HClO4 solution of concentration ≥ 3 M. The above preliminary evidence suggests that at suf-
ciently high perchlorate concentration the following process takes
place.

\[
\text{ClO}_4^- + 7\text{[NiIII(LH)]}^{2+} + 8H^+ \rightleftharpoons 0.5\text{Cl}_2 + 7\text{[NiIII(LH)]}^{4+} + 4\text{H}_2\text{O} \quad (8)
\]

Usually, the aqueous ClO4− ion for kinetic reasons does not exert
its very strong oxidizing power (ClO4− + 7e− + 8H+ = 0.5Cl2(g) + 4H2O, \(E^\circ = 1.392\))20 and most reducing agents persist in-
definitely in acidic perchloric solutions. For instance, the NiIII(cyclam)4+ complex is stable in concentrated perchloric acid
(11.56 M). Thus, the protonated side chain of the presently
investigated complex should play an essential role in the activation
of the ClO4− ion. It is possible that this occurs through the
formation of an ion pair with the –NH3+ group, which activates the
ClO4− ion, at a favorable distance from the reducing metal
center. Reducing tendencies of the metal are obviously required,
as demonstrated by the fact that the analogous CuII scorpionate
complex does not give any reaction even in concentrated perchloric acid.

6. Conclusions. Encircling of a 3d cation by a tetraaza
macrocycle makes its redox behavior more rich, in particular
favoring the access to unusually high, otherwise unstable, oxidation
states (e.g., NiIII). It has been shown that the formation of the
trivalent nickel complex can be made more or less easy by varying
the ring size of the tetraaza ring (the cyclam framework being
the most favorable).7 This work has shown that insertion of a
side chain carrying an amine group on the cyclic framework adds
additional elements of selectivity. In particular, when the side
chain is coordinated to the metal, the attainment of trivalent nickel
is made relatively easier. On the other hand, if the side arm
is protonated, the NiII/NiIII oxidation process becomes substantially
more difficult due to electrostatic repulsive effects. Moreover,
the ammonium group of the pendant arm is able to activate,
through an ion pair interaction, the otherwise kinetically stable
perchlorate ion, which oxidizes the divalent metal center.

Acknowledgment. We thank the Italian Ministry of Education
(M.P.I. 40%) for financial support. Thanks are due to Dr. A.
Buttafava for assistance with ESR measurements.

Registry No. 4, 109151-85-1; 4-5HCl, 109151-86-2; Ni(4)(ClO4)2,
109151-89-5; Ni(4), 109151-90-8; 6, 104395-69-9; 7, 3634-89-7; 8,
109151-87-3.

(17) [Ni(cyclam)]** 0.1 M HClO4 solution frozen at 77 K; \(g_s = 2.22; \)
\(g_L = 2.02.

(18) Taking 2.00 Å for the M–N distance and standard values for the C–C
and C–N distances and bond angles.