Tetra-aza Macrocycles containing a Pyridine Ring. The Oxidation and Reduction Behavior of their Nickel(II) Complexes

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Introduction

Schiff-base condensation of 2,6-diacetylpyridine with the aliphatic triamine dipropylenetriamine (3,3-tri) [1] in presence of Ni(II) ion produces the 14-membered tetra-aza macrocyclic complex *2*, in a reaction which was one of the first synthetic routes to a cyclic chelating agent [2].
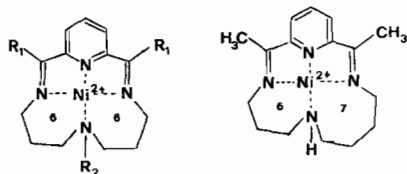
$R_1 = R_2 = H$;
$R_1 = CH_3; R_2 = H$;
$R_1 = R_2 = CH_3$;
1 [14] pydieneN$_4$
2 Me$_2$ [14] pydieneN$_4$
3 Me$_3$ [15] pydieneN$_4$

4 Me$_2$ [15] pydieneN$_4$

In the above complex *2*, Ni(Me$_2$[14]pydieneN$_4$)$^{2+}$ (which was at first named Ni(CR)$^{2+}$) [2], the nickel-(II) ion is shown by X-ray analysis [3] to be coplanar with four chelating nitrogen atoms, arranged approximately in a square. Analogous template reactions with shorter triamines, such as 2,2-tri and 2,3-tri, intended to produce 12- and 13-membered macrocycles, were found not to work [4, 5]. However, nickel(II)-piloted condensation is successful with the longer triamine 3,4-tri, to produce the macrocyclic complex *4* [6]. It is noteworthy that this is the only macrocyclic complex containing a seven-membered chelate ring, formation of which is expected to be highly disfavoured for both enthalpic and entropic reasons. Furthermore, the macrocyclic framework of *2* can be modified, by removing or adding methyl groups to produce *1*, Ni([14]pydieneN$_4$)$^{2+}$ (reaction of 2,6-diformylpyridine with 3,3-tri) [5] and *3*, Ni(Me$_3$[14]pydieneN$_4$)$^{2+}$ (reaction of 2,6-diacetyl-pyridine with H$_2$N(CH$_2$)$_3$N(CH$_3$)(CH$_2$)$_3$NH$_2$) [7], respectively.

Incorporation into a macrocyclic environment greatly modifies the electronic structure of the nickel-(II) ion, which then displays unusually rich oxidation and reduction behavior [8]. For instance, the otherwise unusual +3 state can be easily achieved and many Ni(III) tetra-azamacrocyclic complexes have been chemically [9, 10] and electrochemically [8, 11–13] prepared. A great deal of work has been done on the electrochemical properties of Ni(II) complexes with macrocycles containing all imine and/or amine nitrogen atoms [8] and considerable efforts have been made to correlate redox potentials with the structural features of the coordinating ligand [8, 13, 14]. An electrochemical study has been carried out on Ni(Me$_2$[14]pydieneN$_4$)$^{2+}$, *2*, and on its derivatives having higher and lower degrees of unsaturation [15].

We report here the electrochemical behavior, in acetonitrile 0.1 *M* Et$_4$NBF$_4$, at 25 °C, of *1–4* with the aim of evaluating the effects on the redox properties of the Ni(II) complexes of this novel series of macrocycles containing a pyridine ring produced by modifications of the ligand framework, such as i) insertion of methyl groups on carbon and nitrogen atoms, or ii) expansion of a chelate ring.

Experimental

Materials

2,6-diacetylpyridine (Aldrich Europe) was recrystallized from absolute ethanol. Dipropylenetriamine and 3,3'-bis(propylamine)-methylamine were obtained from Fluka and purified through distillation under reduced pressure. 2,6-diformylpyridine (K & K) and 3-propylamine-N-butylamine (3,4-tri) (Ega Chemie) were used as supplied. All the complexes were obtained as perchlorates and were prepared through a procedure based on the published methods [2]. We have found that the yield improves remarkably when mild conditions (low concentration of reactants and low temperature) are employed. In a typical preparation, a water/ethanol solution (1/1), made 10^{-2} in NiCl$_2$, dicarbonylpyridine and

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TABLE I. Electrochemical Behavior of Ni(macrocycle)(ClO$_4$)$_2$ Complexes in Acetonitrile, 0.1 M Et$_4$NBF$_4$, at 25 °C. Electrode Potentials (V) *vs.* Ag/AgNO$_3$ 0.01 M, 0.1 M Et$_4$NBF$_4$.

Complex	Formula	+2 → +3[a]	+2 → +1[b]	+1 → 0[b]
Ni([14]pydieneN$_4$)$^{2+}$	(1)	+1.143	−0.765	−1.325
Ni(Me$_2$[14]pydieneN$_4$)$^{2+}$	(2)	+1.064	−0.909	−1.490
Ni(Me$_3$[14]pydieneN$_4$)$^{2+}$	(3)	+1.214	−0.890	−1.508
Ni(Me$_2$[15]pydieneN$_4$)$^{2+}$	(4)	+1.357	−0.980	−1.508

[a]Measured at the platinum electrode, ±0.005 V.   [b]Measured at the mercury electrode, ±0.005 V; values obtained at the platinum microsphere (CV) coincide within ±0.010 V.
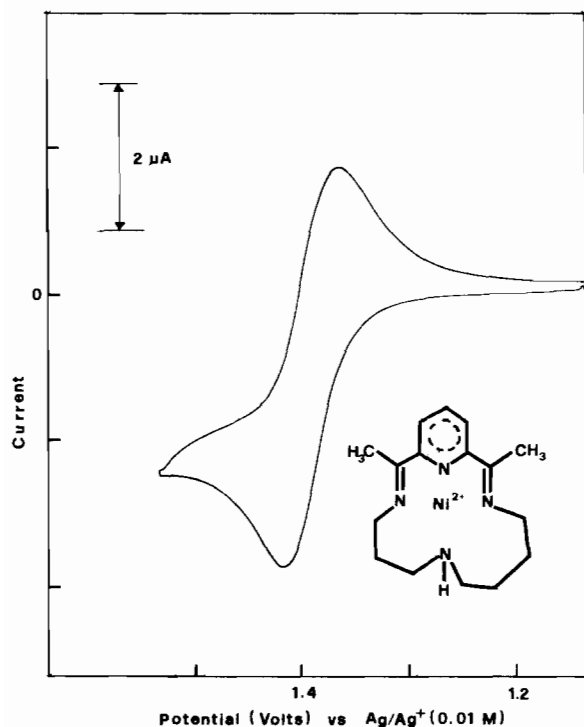

Fig. 1. CV response, at the platinum microsphere, for a 10^{-3} M solution of Ni(Me$_2$[15]pydieneN$_5$)(ClO$_4$)$_2$, *4*, in acetonitrile 0.1 M Et$_4$NBF$_4$, at 25 °C. Potential scan speed: 100 mV s^{-1}.

triamine, is maintained at 60 °C for 2 hours with stirring. Stirring is continued at room temperature for 16–20 hours. The brown solution is filtered and reduced to 1/20 of its original volume through rotovaporation. Addition of an equal volume of 7 M NaClO$_4$ solution causes precipitation of the complex salt, which is recrystallized from water. Complexes are obtained as dihydrates and are dehydrated when kept *in vacuo* overnight over P$_4$O$_{10}$ at 60 °C; Complete dehydration is required in order to obtain reproducible polarographic response.

Electrochemistry

Acetonitrile (Erba, RPE) was distilled consecutively from CaH$_2$, P$_4$O$_{10}$, CaH$_2$ and kept over molec-

ular sieves in a nitrogen atmosphere. Et$_4$NBF$_4$ (Fluka, *Purissimum*) was dried over P$_4$O$_{10}$ *in vacuo* for 1 week. Measurements were performed with the Electrochemolab System (Amel, Milan), consisting of a potentiostat (552/MWR) and a function generator (Model 566) connected through a multi-function interface (Model 563). Experiments were performed in a three-electrode H-type cell, thermostatted at 25 ± 0.05 °C, under nitrogen. The reference electrode was a silver coil immersed in a solution 0.01 M in AgNO$_3$ and 0.1 M in Et$_4$NBF$_4$. Platinum electrodes were pretreated through immersion in chromic acid, washing with water and solvent and anodizing at a small positive potential. A platinum foil was used as auxiliary electrode. Nitrogen used to deaerate solutions was further purified by passing through consecutive columns filled with BASF R-131 Catalyst and molecular sieves (to remove the last traces of oxygen and water, respectively).

Results and Discussion

Oxidation Behavior

All the complexes considered undergo a reversible one-electron oxidation at the platinum electrode, as shown by the usual electrochemical tests: CV voltammograms (Fig. 1) with unitary i$_p$(anodic)/i$_p$(cathodic) ratio and i$_p$ proportional to the square root of the potential scan speed; symmetrical AC peaks having half-peak width of 90 mV; S-shaped voltammograms with non stationary electrodes (rotating or vibrating platinum wire) for which the (E$_{3/4}$–E$_{1/4}$) difference ranged within 56–60 mV. The E$_{1/2}$ values obtained by these different techniques were found coincident within the experimental error and are reported in Table I. The one-electron stoichiometry was definitely established by coulometric experiments.

This behavior is general for all nickel(II) complexes with tetra-aza macrocycles and the oxidation product is a true Ni(III) species, as shown by the ESR spectra which are typical for a low-spin d^7 chromophore, NiL(CH$_3$CN)$_2^{3+}$ [8].
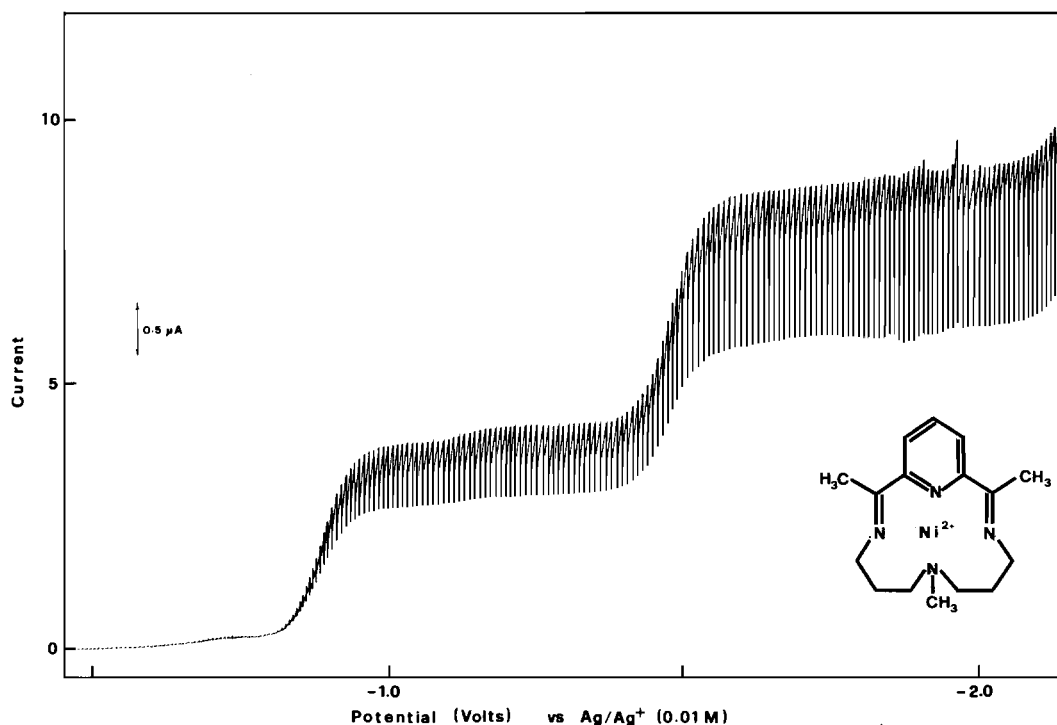
Fig. 2. Polarographic response for a 10^{-3} *M* solution of Ni(Me₃[14]pydieneN₅)(ClO₄)₂ in acetonitrile 0.1 *M* Et₄NBF₄, at 25 °C.

Noticeably, Ni(Me₂[14]pydieneN₄)²⁺ is oxidized at a lower potential than the complex with the parent unsubstituted ligand Ni([14]pydieneN₄)²⁺ (see Table I), *i.e.* insertion of two methyl groups in the carbon backbone apparently makes oxidation to Ni(III) easier. This is in contrast with what has been found [8] for Ni(II) complexes of cyclic tetramines for which progressive introduction of methyl groups on the sp³ carbon atoms was found to increase the oxidation potential: nickel(II) tetra-aza macrocyclic complexes in acetonitrile have a tetragonally distorted stereochemistry [7] and electron abstraction to produce the low-spin d⁷ species causes a drastic shortening of the axial Ni–NCCH₃ bonds [8], leading to steric hindrance by alkyl substituents on the aliphatic chains. On the other hand, in Ni(Me₂[14]-pydieneN₄)²⁺ methyl groups are bound to the sp² carbon atoms involved in the imine bonds and lie in the NiN₄ plane, *i.e.* in a position of minimized steric hindrance to apical ligands; thus, they are expected not to interfere with the oxidation process. Moreover, such methyl groups are supposed to increase, through 'inductive effect', the electron density on the adjacent nitrogen donor atoms, thus making electron abstraction from the encircled Ni(II) ion less difficult.

On the same basis, one would predict that introduction of a further methyl group directly on the amine nitrogen atoms, as in Ni(Me₃[14]pydiene-N₄)²⁺, *3*, would further enrich the negative charge

on the coordinated metal ion and further decrease the value of the oxidation potential. On the contrary, the electrode potential is remarkably increased with respect to Ni(Me₂[14]pydieneN₄)²⁺,*2*. The apparent paradox can be explained by considering that the methyl group on the amine nitrogen atom is stereochemically active and can sterically resist the shortening of the axial Ni–NCCH₃ bonds, which is associated with the Ni^{II} → Ni^{III} change. Therefore, the eventual benefit from the increase of the electron density is more than compensated for by the steric effects introduced by the alkyl group and the oxidation process is made comparatively more difficult. It is noteworthy that the difference between the electrode potentials of *3* and *2* (150 mV) is of the same order of magnitude as the increase evaluated for the insertion of a sterically active CH₃ group on a sp³ carbon atom, observed with saturated tetra-aza macrocycles (180 mV) [8]. It should be noted that up to now Ni(Me₃[14]pydieneN₄)²⁺ is the only macrocyclic complex having an alkyl substituted nitrogen atom that has been investigated electrochemically.

Expansion of one of the two six-membered chelate rings of *2* to a seven membered ring, to produce *4*, generates a prodigious increase of the oxidation potential (see Table I). Among the more than thirty nickel(II) tetra-aza macrocyclic complexes synthesized and investigated up to date, Ni(Me₂[15]-pydieneN₄)³⁺ is the most strongly oxidizing. In a general sense, the comparatively easy preparation of

Ni(III) macrocyclic complexes depends on the strong in-plane interactions of the four nitrogen atoms, which make quite high the energy of the metal orbital from which the electron is abstracted. This energy level becomes higher (and the oxidation process easier), as the geometrical arrangement of the co-planar donor atoms approaches the square. The presence of the unusual seven-membered chelate ring in *4* is expected to cause severe deviations from the preferred square coordinate geometry. This should reduce the intensity of Ni–N interactions and increase the value of the oxidation potential. Expansion from a 14- to a 15-membered ligand was found to produce similar effects also in the oxidation of Ni(II) complexes of cyclic tetramines [8, 13].

5   **6**   **7**
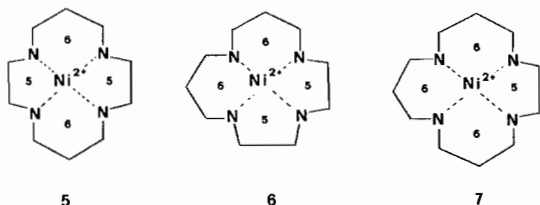
$E(+2 \rightarrow +3) = +0.70 V$ [13]
$E(+2 \rightarrow +3) = +0.84 V$ [13]
$E(+2 \rightarrow +3) = +1.01 V$ [13]

However, in this case the change from the 14-membered complexes *5* or *6* to the 15-membered *7* was achieved through expansion of a five-membered chelate ring. Furthermore, it must be considered that the $+2 \rightarrow +3$ change involves a decrease in size of the encircled metal ion and steric constraints experienced by the larger ligand, which is forced to contract its aperture, further disfavour the oxidation process.

Reduction Behavior

All the complexes under investigation give two one-electron reversible reduction steps at both platinum and mercury electrodes. Electrochemical response shows the simplicity of the electron transfer: slope of 60 mV (DC) (Fig. 2) and half-peak width of 90 mV (AC) for experiments at DME; reversible CV curves for stationary mercury and platinum electrodes. In the previous electrochemical study on $Ni(Me_2[14]pydieneN_4)^{2+}$, *2* [15], the electron taken up on the first reduction step was assumed to delocalize over the diene system: ESR spectra of the

electrochemically produced NiL^+ species gave an isotropic g value [8], so the species must be considered a Ni(II)–ligand radical complex. On the other hand, the second electron was considered to drop into an orbital having a predominantly metal character [15]. From the strict similarity of the electrochemical response, analogous assignments can be extended to the other macrocyclic complexes of the same family. The interpretation of the trend of the reduction data (see Table I) is not straightforward: the most striking feature is the remarkably easier reduction, at both first and second steps, of $Ni[14]\text{-}pydieneN_4)^{2+}$, 1, compared to the homologous *2–4* complexes, *i.e.* both reduction processes seem to be particularly sensitive to the introduction of methyl groups on the sp^2 carbon atoms of the imine bonds (which makes reduction more difficult), but are much less sensitive to the methylation of the amine nitrogen and to enlargement of the macrocyclic aperture.

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