Electroactive Films of Nickel(II)–Cyclam (1,4,8,11-tetra-azacyclotetradecane) Covalently Attached to Polypyrrole

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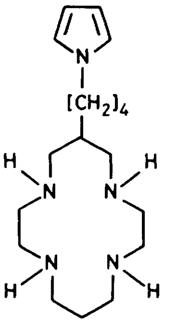
A monomeric molecule consisting of a nickel(II)–cyclam derivative covalently linked to a pyrrole subunit has been synthesized and characterized; its electropolymerization results in an adhesive conducting film on glassy carbon.

Since the first report on electrochemical coating of electrodes by conducting films of polypyrrole,[1a] electrode surface deposition of redox polymers has received considerable attention. In spite of the much lower conductivity of N-substituted polypyrrole films as compared to polypyrrole itself,[1b] one of the most appealing means of incorporating a catalytic species into an electroactive film[2] is by covalently linking the molecular electrocatalyst to pyrrole *via* its nitrogen atom. Recent work along these lines includes ferrocene,[3] viologens (*N*,*N*′-dialkyl-4,4′-bipyridinium salts),[4a] 2,2′-bipyridine complexes of ruthenium(II),[4b–c,5] rhenium(I),[4d] or copper(II),[6] and anthraquinone[7] modified polypyrrole.

In view of the interesting electrocatalytic properties of Ni^{II}(cyclam)$^{2+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) and analogous complexes,[8] we have synthesized a cyclam molecule bearing a pendant pyrrole unit (**1**), whose nickel(II) complex is the precursor to electroactive films incorporating a Ni^{II}(cyclam)$^{2+}$ derivative.

Compound (**1**) was prepared from a laterally functionalized molecule previously reported by Tabushi *et al.*[9] 3-(4-Amino-n-butyl)-1,5,8,12-tetra-azacyclotetradecane[9] (1.5 mmol) was treated with *cis*-but-2-ene-1,4-diol (4.0 mmol) in the presence of Pd black (25 mg), following a previously reported synthetic method.[10] The reaction mixture was magnetically stirred at 120 °C under argon for 45 h. After chromatographic separation (Al_2O_3; ethyl acetate–methanol) of the crude product, (**1**) was obtained in 24% yield as a white glassy solid. Compound (**1**) was characterized by mass spectroscopy (M^+, m/z 321) and by ^1H n.m.r. spectroscopy in CD_3OD (characteristic pattern of the pyrrolic subunit showing two multiplets at δ 6.02 and 7.66).

The chemical stability of (**1**) is poor whereas its nickel(II) complex can be stored in air, at room temperature, for months. This complex was prepared in good yield by mixing stoicheiometric amounts of (**1**) and $Ni(ClO_4)_2·6H_2O$ in MeOH. After filtration and drying *in vacuo*,† a yellow powder of $[(\mathbf{1})Ni^{2+}](ClO_4)_2$ was obtained. The complex gave good elemental analyses (C,H,N). Its electronic spectrum is similar to that of Ni(cyclam)$^{2+}$, showing a low intensity band around 440 nm. Cyclic voltammetry (c.v.) measurements lead to redox potential values very close to those of Ni(cyclam)$^{2+}$. In MeCN, $E°(Ni^{III}/Ni^{II}) = +0.98$ V *vs.* S.C.E. (standard calomel electrode) and $E°(Ni^{II}/Ni^{I}) = -1.41$ V for $(\mathbf{1})Ni^{2+}$, whereas for Ni(cyclam)$^{2+}$, $E°(Ni^{III}/Ni^{II}) = +1.00$ V and $E°(Ni^{II}/Ni^{I}) = -1.47$ V.[11] For $(\mathbf{1})Ni^{2+}$ irreversible and multi-electronic oxidation of the pyrrolic group occurs at 1.35 V, a value close to that found for other N-substituted pyrroles.[1b]



(**1**)

Electropolymerization of $(\mathbf{1})Ni^{2+}$ was performed in MeCN by repeated cyclic scanning of potential (0.4—1.2 V) on a glassy carbon electrode. Typical results are shown in Figure 1a.

The main electrochemical process corresponds to the Ni^{III}/Ni^{II} couple. The increase in size of c.v. peaks for the latter clearly demonstrates the formation and growth of a polymer film on the electrode surface. After eight scans, the electrode was rinsed copiously with solvent and dipped into fresh MeCN solution. The c.v. pattern thus obtained is shown in Figure 1(b). The Ni^{III}/Ni^{II} peak separation is ~100 mV, depending on the film thickness. Many scans can be repeated without any change of the c.v. curve.

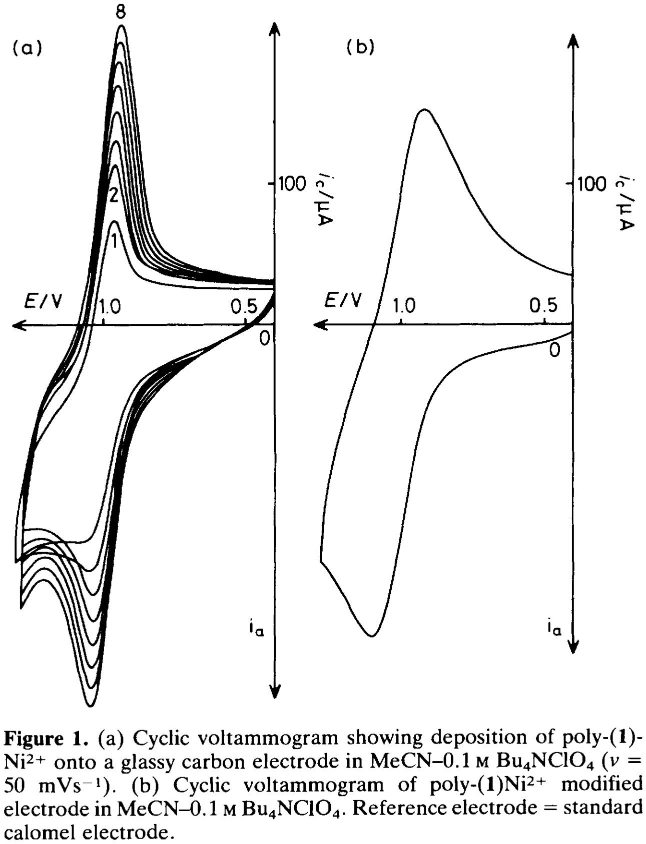


Figure 1. (a) Cyclic voltammogram showing deposition of poly-(**1**)-Ni^{2+} onto a glassy carbon electrode in MeCN–0.1 M Bu_4NClO_4 (ν = 50 mVs^{-1}). (b) Cyclic voltammogram of poly-$(\mathbf{1})Ni^{2+}$ modified electrode in MeCN–0.1 M Bu_4NClO_4. Reference electrode = standard calomel electrode.

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† **Caution:** Handing of perchlorate salts of amine complexes is particularly dangerous.

The blue film adheres strongly to the electrode surface. The peak current intensity is proportional to the potential sweep rate over a wide range (10—150 mV/s), as expected for an electroactive compound deposited on the electrode surface. The estimated surface coverage is $\sim 2 \times 10^{-8}$ mol cm^{-2}.

Unfortunately, the film becomes insulating as soon as a cathodic potential is applied, unlike other recent examples.[4] It is noteworthy that the present example deals with a non-aromatic electroactive species. The Ni^{II}/Ni^{I} couple involves a metal localized redox orbital, whereas for previous reports[4] the presence of bipyridine moieties favours ligand localized redox processes. The structural difference might be related to the higher conductivity of the latter films under cathodic potentials as compared to those of our systems. The nickel(II) cyclam modified polypyrrole film does not lead to redox processes involving the Ni^{II}/Ni^{I} couple, preventing its use in electroreductive reactions. The difficulty arising from the low conductivity of the film could not be circumvented by copolymerizing (**1**)Ni^{2+} and pyrrole, although an electroactive film was formed in the anodic region more easily than for that made from (**1**)Ni^{2+} alone.

The reversibility of the Ni^{III}/Ni^{II} couple might allow the present polypyrrolic film to be used in oxidative electrocatalysis.

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