Novel Electrochemical Behaviour of a Nickel(n)–13-Membered Macrocyclic Tetra-amine effected by a Pendent Phenol

Eiichi Kimura,* Tohru Koike, Keiji Uenishi, and Richard B. Davidson

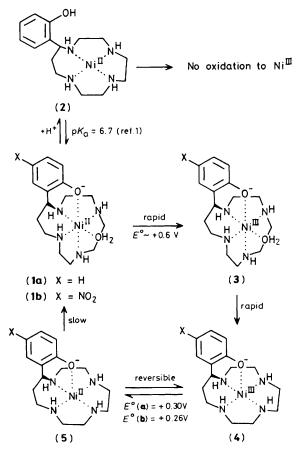
Department of Medicinal Chemistry, Hiroshima University School of Medicine, Kasumi, Hiroshima 734, Japan

The *cis*-macrocyclic configuration in the phenol-pendant-[13]aneN₄ [11-(2'-hydroxyphenyl)-1,4,7,10-tetra-aza-cyclotridecane] complex with Ni^{III} rapidly rearranges to a 'square planar' form upon oxidation to Ni^{III} at *ca.* +0.6 V *vs.* saturated calomel electrode (s.c.e.) with a subsequent occurrence of a new reversible Ni^{III/III} process at +0.30 V for the macrocycle with a pendent phenol and +0.26 V *vs.* s.c.e. for that with a pendent *p*-nitrophenol; the thus generated short-lived high-spin square-planar Ni^{III} complex returns to the initial folded Ni^{III} complex with a half-life time of 11.4 s (for the *p*-nitrophenol macrocycle) at 25 °C.

The crystal structure of the Ni^{II}-phenol-pendant-[13]aneN₄ complex (1a) has revealed a *cis* configuration for the [13]aneN₄ macrocycle with strong axial interaction by the phenolate.¹

The cyclic voltammograms (c.v.s) (Figure 1) of (1a) and (1b) (*p*-nitrophenol-pendant) in $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ aqueous solution at 25 °C have disclosed novel electrochemical behaviour. The *p*-nitrophenol ligand is robust to oxidation, so that we could obtain the most precise and reproducible c.v.s with (1b). The new *p*-nitrophenol macrocycle [m.p. 189 °C (decomp.), as 4HCl salt] was synthesized in the same manner as before,² using 6-nitrocoumarin and 1,8-diamino-3,6-diazaoctane instead of coumarin and 1,9-diamino-3,7-diazanonane.

Both (1a) and (1b) show only one peak at ca. +0.6 V vs. saturated calomel electrode (s.c.e.) in the first anodic sweep from 0 to +1.0 V. However in the back cathodic sweep, the corresponding reduction wave is much weaker than antici-



Scheme 1

pated for a reversible electrode process, and moreover new waves appear at +0.27 V for (1a) and +0.23 V vs. s.c.e. for (1b) (see curve c in Figure 1). In the second scan, oxidation peaks corresponding to these reduction peaks emerge at +0.33 V and +0.29 V vs. s.c.e., respectively. In successive scans, the height of the new coupled waves at ca. +0.3 V increases, while the peaks at ca. +0.6 V decrease. After seven or eight cycles, no further c.v. changes were observed. Referring to Scheme 1, the first anodic peak at ca. +0.6 V (representing one electron oxidation, see curve b in Figure 1) is assigned to the Ni^{II} (1) \rightarrow Ni^{III} (3) process in the folded configuration of macrocycle. However, owing to the d⁷ electronic effect and its small size, Ni^{III} would rather be in the *trans* N₄ state (4) than the *cis* N₄ state (3) and thus the rapid conversion from (3) into (4) would occur. Molecular models indicate that the *cis* to *trans* rearrangement is easy.

Application of a constant potential of +0.8 V vs. s.c.e. yields the intense yellow colour of (4) [λ_{max} 413 nm, $\varepsilon 4.3 \times 10^3$ for (4a), λ_{max} 386 nm, $\varepsilon 2.3 \times 10^4$ for (4b)], whose c.v. shows a redox wave at ca. +0.3 V (representing 1e⁻ redox process, see curve a in Figure 1), but none at ca. +0.6 V. The middle peak potentials $E_{1/2}$ of +0.30 V (4a) and +0.26 V vs. s.c.e. (4b) are a little smaller than that at +0.35 V vs. s.c.e. (at 25 °C, 0.5 M Na₂SO₄, and pH 8) measured for Ni^{II/III} in the phenol-pendant-[14]aneN₄ where the macrocycle retains one square-planar configuration (as shown by only one reversible

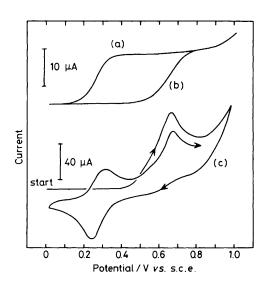


Figure 1. Rotating glassy carbon disk electrode current-potential curves at 25 °C, an electrode rotation rate of 2400 r.p.m., and a scan rate of 10 mV s⁻¹ with 0.5 m Na₂SO₄ as supporting electrolyte, (a) for 1 mm (4b) at pH 6 and (b) for 1 mm (1b) at pH 7.0; (c) is the cyclic voltammogram for the same solution as (b) on a glassy carbon rod electrode at a scan rate of 100 mV s⁻¹.

wave at +0.35 V).³ Hence we assign a similar Ni^{II/III} process, (4) \rightleftharpoons (5), in a tighter square-planar [13]aneN₄ geometry. The Ni^{III}-phenol-free-[14]aneN₄ has a similar intense charge transfer absorption at λ_{max} 370 nm, ε 6.0 × 10³.⁴ The e.s.r. spectra of the planar-Ni^{III} species (4a) and (4b) in frozen solutions at 77 K, both with $g_{\perp} = 2.17$ and $g_{\parallel} = 2.02$, are almost identical to that found for the Ni^{III}-phenol-pendant-[14]aneN₄ homologue ($g_{\perp} = 2.18$, $g_{\parallel} = 2.03$)³ and for Ni^{III}-[14]aneN₄ ($g_{\perp} = 2.23$, $g_{\parallel} = 2.03$).⁴⁻⁶ Thus, we have for the first time identified the high-spin Ni^{II} in a *trans*-[13]aneN₄ arrangement with (5).

The observed reversible nature of the Ni^{II/III} couples in the square-planar [13]aneN₄ suggests appreciable stability of the possible high-spin, square-planar Ni^{II} complex (5). It is to be emphasized that without the axial phenolate co-ordination, low-spin Ni^{II} in square-planar [13]aneN₄ {*e.g.* (2) or pendant-free-[13]aneN₄ complex} does not produce such a Ni^{II/III} redox c.v. at all at < +0.7 V vs. s.c.e. Owing to the high kinetic barrier imposed by the rigid macrocyclic configuration, (5) could survive during the time scale of cyclic voltammetry. The expected thermodynamic downhill conversion into the original, more stable folded isomer (1b) was measured in the c.v. scan of (4b) \rightleftharpoons (5b). The ratio *i*(anode): *i*(cathode) was found to decrease in proportion to the time (defined by τ in ref. 7) required to scan from the $E_{1/2}$ (+0.26 V) to the switching potential (0 to -0.4 V vs. s.c.e.), as theoretically derived for a

process involving reversible charge transfer (ox \rightleftharpoons red), followed by an irreversible chemical reaction (red \rightarrow red').⁷ The constant value of $6.1 \times 10^{-2} \text{ s}^{-1}$ (pH-independent for pH 5—7 at 25 °C and 0.5 M Na₂SO₄) thus corresponds to the first order rate constant $k_{\rm f}$ for conversion of (**5b**) (red) to (**1b**) (red'). Indeed, (**5b**) very rapidly and quantitatively goes back to (**1b**) upon reduction of (the electrochemically generated) (**4b**) by applying a constant potential of 0 V vs. s.c.e.

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