

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 6.0×10^3 .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 $i(\text{anode}) : i(\text{cathode})$ 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_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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