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Control of the redox activity of anthraquinone through an appended nickel(II)–cyclam side chain. A two-site three-electron redox system

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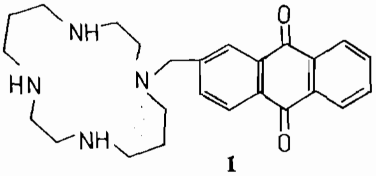
Abstract

The conjugate system **1** has been prepared through reaction of 2-chloromethylanthraquinone with a five-fold excess of cyclam in chloroform at room temperature. Reaction of **1** with $NiX_2 \cdot 6H_2O$ (X = Cl, ClO_4) gave the corresponding $Ni(1)X_2$ complexes, in which the metal centre has been incorporated by the tetraaza-macrocyclic subunit. The redox behaviour of the nickel(II) complexes has been investigated in a CH_2Cl_2 solution of 0.1 M Bu_4NX, by voltammetric techniques. Two-phase reduction of the quinone subunit of the $Ni(1)X_2$ complex in CH_2Cl_2 by aqueous Cr^{II} takes place at a rate much higher than that observed for the simple anthraquinone molecule, but the reduced conjugate system partitions between CH_2Cl_2 and water.

The novel conjugate system **1**, 1-anthraquinonyl-1,4,8,11-tetrazacyclotetradecane ($cyaqO_2$), has been synthesized, assembling the classical organic redox system anthraquinone [1] and the cyclam subunit, able to incorporate transition metal ions and to promote their redox activity [2], has been synthesized.



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The aim of this work was to produce a two-site multi-electron redox system, in which two proximate redox centres could mutually control each other, which can be envisaged as a versatile carrier for the transport of electrons across liquid membranes. $cyaqO_2$ has been obtained through reaction of 2-chloromethylanthraquinone [3] with a five-fold excess of cyclam [4] in $CHCl_3$ (3 days, at room temperature). After solvent rotovaporation, $cyaqO_2$ was separated from excess cyclam through extraction by cold benzene. $cyaqO_2$ was obtained as a yellow solid, which was recrystallized from chlorobenzene (m.p. 138–140 °C; ^1H NMR in $CDCl_3$: 1.8 (m, 4H: CH_2 of cyclam not directly bonded to nitrogen atoms), 2.75 (m, 19H: NH and all other CH_2 of cyclam), 3.7 (s, 2H: CH_2 bridge), 7.25 (s, 1H: anthraquinonyl subunit, aq), 7.75 (m, 3H: aq), 8.25 (m, 3H: aq)). Reaction with $NiX_2 \cdot 6H_2O$ (X = Cl, ClO_4) in refluxing ethanol gave the $Ni(cyaqO_2)Cl_2$ (purple, high-spin) and $Ni(cyaqO_2)(ClO_4)_2$ (yellow, low-spin) complexes, which are soluble in apolar or poorly polar non-coordinating solvents (C_6H_6, CH_2Cl_2, $CHCl_3$) and insoluble in water.

The redox behaviour of the above complexes was investigated by voltammetric techniques in a CH_2Cl_2 solution of 0.1 mol dm^{-3} in Bu_4NX, at 25 °C, using a platinum sphere as the working electrode.

In Fig. 1 the solid line displays the differential pulse voltammetric profile of a 5×10^{-4} mol dm^{-3} solution of the $Ni^{II}(cyaqO_2)(ClO_4)_2$ complex, while the dashed line profile was obtained with a reference solution of 5×10^{-4} mol dm^{-3} Ni^{II}(*N*-cetylcyclam)$(ClO_4)_2$** and 5×10^{-4} mol dm^{-3} 2-methylanthraquinone ($MeaqO_2$). For both profiles, the more anodic one-electron peak corresponds to the Ni^{II} to Ni^{III} oxidation process. $MeaqO_2$ (dashed line) presents two distinct and reversible one-electron peaks, whereas for the $Ni(cyaqO_2)(ClO_4)_2$ complex (solid line) the uptake of the second electron by the quinone fragment anticipates the cathodic discharge. Similar electrochemical behaviour is displayed by the $Ni^{II}(cyaqO_2)Cl_2$ system, in a 0.1 mol dm^{-3} solution

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***N*-Cetylcyclam: 1-hexadecyl-1,4,8,11-tetraazacyclotetradecane. Its Ni^{II} complexes are soluble in apolar and poorly polar media, such as CH_2Cl_2 [5].

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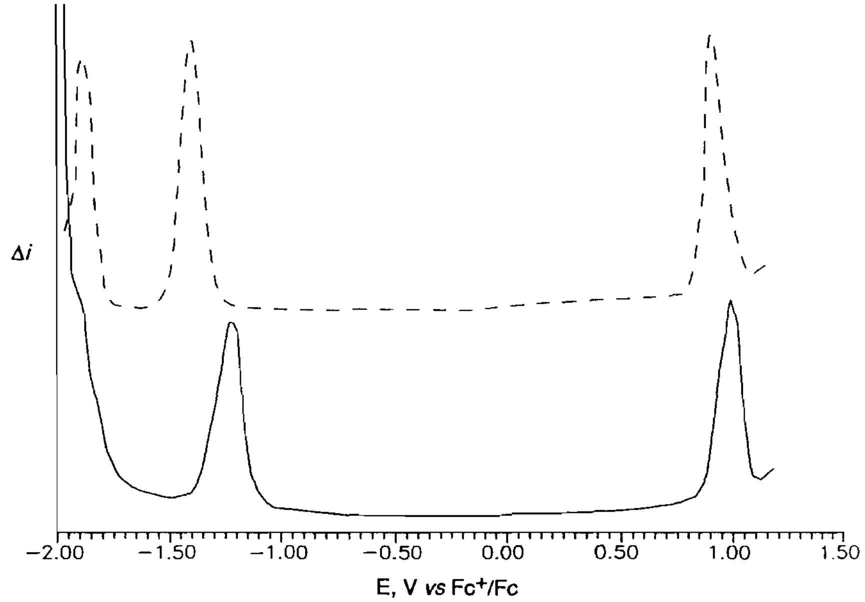

Fig. 1. Differential pulse voltammetry profiles of: (——) a CH_2Cl_2 solution of 5×10^{-4} mol dm^{-3} $Ni^{II}(cyaqO_2)(ClO_4)_2$ and 0.1 mol dm^{-3} Bu_4NClO_4; (-----) a CH_2Cl_2 solution of 5×10^{-4} Ni^{II}(*N*-cetylcyclam)$(ClO_4)_2$, 5×10^{-4} mol dm^{-3} Meaq and 0.1 mol dm^{-3} Bu_4NClO_4. Potential scan rate: 5 mV s^{-1}, pulse voltage 25 mV, 25 °C. The scale of potential is calibrated vs. the internal Fc^+/Fc reference couple.

of Bu_4NCl. $E_{1/2}$ values pertinent to each redox event are reported in Table 1.

The following points should be noted: (i) for a given anion (chloride or perchlorate), oxidation of the metal centre is slightly more difficult in the conjugate system (more positive Ni^{III}/Ni^{II} potential) than in the *N*-cetylcyclam complex, probably due to a partial electron withdrawing effect exerted by the anthraquinonyl substituent; this effect is smaller when axial positions are held by the more electron donating Cl^- ions (+30 mV, to be compared to +70 mV for the perchlorate analogue*; (ii) the first one-electron reduction of the anthraquinone fragment is easier (less negative potential) in the conjugate system than in the individual molecule: this could result from the stabilizing effect arising from the electrostatic interaction between the negatively charged organic subunit aqO_2^- and the neighbouring Ni^{II} metal centre. The advantage is substantially greater for the $Ni^{II}(cyaqO_2)(ClO_4)_2$ system (−170 mV) than for the $Ni^{II}(cyaqO_2)Cl_2$ system (−60 mV), probably due to the lower charge shielding effect exerted on the Ni^{II} cation by the poorly donating axially bound ClO_4^- ions, compared with Cl^- ions.

TABLE 1. Half-wave potential values measured in CH_2Cl_2 solution of 0.1 mol dm^{-3} Bu_4NX, at 25 °C (V, vs. Fc^+/Fc)[a]

	Ni^{III}/Ni^{II}	aqO_2/aqO_2^-
Ni(*N*-cetylcyclam)Cl_2[b]	0.17	
Ni(*N*-cetylcyclam)$(ClO_4)_2$[b]	0.92	
$MeaqO_2(Bu_4NCl)$[c]		−1.43
$MeaqO_2(Bu_4NClO_4)$[c]		−1.42
$Ni(cyaqO_2)Cl_2$[c]	0.21	−1.37
$Ni(cyaqO_2)(ClO_4)_2$[c]	0.99	−1.25

[a] ±2 mV. [b] Ref. 5. [c] This work.

Solubility in poorly polar solvents and insolubility in water, as well as the rich and concerted redox behaviour, suggests that the $Ni^{II}(cyaqO_2)(ClO_4)_2$ and $Ni^{II}(cyaqO_2)Cl_2$ systems may be considered as carriers for the transport of electrons across liquid membranes. Preliminary two-phase experiments were performed in a 1 cm spectrophotometric cuvette, filled with 2.0 cm^3 of a CH_2Cl_2 solution, a 5×10^{-4} mol dm^{-3} solution of $MeaqO_2$ and with 1.0 cm^3 of an aqueous solution of 0.1 mol dm^{-3} Cr^{II} and 1 mol dm^{-3} $HClO_4$. Spectra of the non-aqueous layer, magnetically stirred at a constant rate, were taken at defined time intervals. It was observed that the UV absorption band of the $MeaqO_2$ chromophore,

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*The very dramatic effect of the inorganic anion (chloride or perchlorate) on the potential associated to the one-electron oxidation of the Ni^{II} centre in both *N*-cetylcyclam [5] and $cyaqO_2$ complexes reflects the much higher ligand field stabilization effect exerted by the axially coordinated Cl^- anions on the low-spin Ni^{III} cation, in the octahedrally elongated *trans*-diacido tetraaza-macrocyclic complexes, if compared with the ClO_4^- anions.

centred at 328 nm, slowly decreases with time, whereas a new composite band forms and develops in the 350–450 nm range, pertinent to the reduced 2-methyl-9,10-dihydroxyanthracene molecule, Meaq$(OH)_2$ [6]. Figure 2 reports the variation with time of the percent concentration of MeaqO_2 in the CH_2Cl_2 layer, calculated through the intensity of the 328 nm band. After 16 h, when the experiment was interrupted, 50% of MeaqO_2 had been reduced, through the half-reaction: Meaq$O_2 + 2e^- + 2H^+ =$ Meaq$(OH)_2$ [7].

The same experiment was performed using a CH_2Cl_2 solution of the Ni^{II}(cyaqO_2)$(ClO_4)_2$ complex: decrease of the intensity of the band at 328 nm is much faster than for the reference system (see Fig. 2), indicating an extremely higher rate of the two-phase reduction process, which is complete in about 2 h. The dramatic rate enhancement is ascribed to the presence of the hydrophilic metal–cyclam subunit, which is believed to facilitate the approach of the hydrophobic anthraquinone moiety to the CH_2Cl_2/water interface, favouring the interaction with the aqueous reducing agent. This seems a very promising property which could enhance the rate of an anthraquinone mediated transport of electrons across liquid membranes [8]. However, detection of the band at 350–450 nm in the aqueous layer in the cuvette indicated that the species Ni^{II}(cyaq$(OH)_2$)$^{2+}$, after the facilitated two-phase reduction, is distributed between CH_2Cl_2 and water ([water]/[CH_2Cl_2] ratio = 60:40), owing to the combined hydrophilic effects of the metal centre and of the –OH groups. This prevents the use of Ni^{II}(cyaqO_2)X_2 systems as electron carriers in liquid membranes (analogous behaviour was observed with the Ni^{II}(cyaqO_2)Cl_2 complex). Design of supramolecular multi-electron carriers, assemblying: (i) a tetraaza-macrocyclic metal centre, (ii) the anthraquinone subunit and (iii) an appended definitively lipophilic group able to anchor the system to the liquid membrane, is currently being investigated in our laboratory.

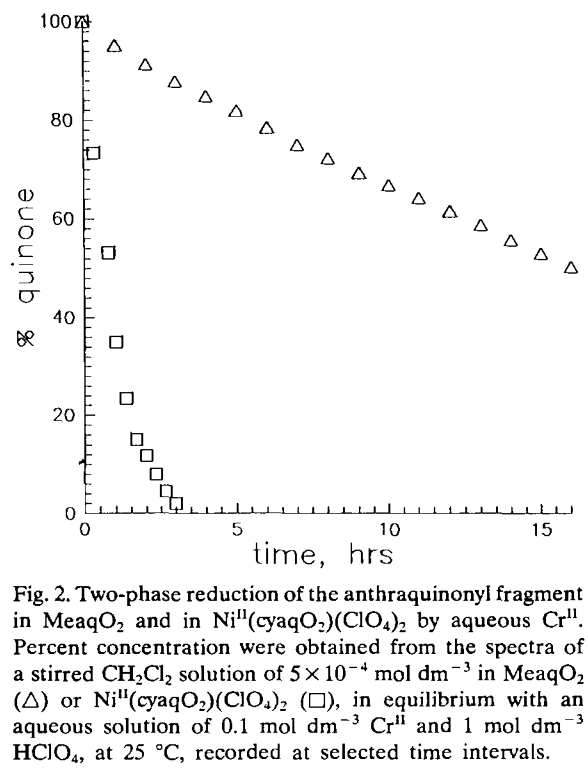

Fig. 2. Two-phase reduction of the anthraquinonyl fragment in MeaqO_2 and in Ni^{II}(cyaqO_2)$(ClO_4)_2$ by aqueous Cr^{II}. Percent concentration were obtained from the spectra of a stirred CH_2Cl_2 solution of 5×10^{-4} mol dm^{-3} in MeaqO_2 (△) or Ni^{II}(cyaqO_2)$(ClO_4)_2$ (□), in equilibrium with an aqueous solution of 0.1 mol dm^{-3} Cr^{II} and 1 mol dm^{-3} $HClO_4$, at 25 °C, recorded at selected time intervals.

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