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Unusual reductive behaviour of a *trans*-$NiI_2(RNC)_2$ complex at mercury and platinum electrodes

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Abstract

Electrochemical reactions of $NiI_2(RNC)_2$ ($R = 2,6\text{-}Me_2C_6H_3$) differed according to electrode materials. At a platinum electrode the reaction was shown by cyclic voltammogram to proceed in the usual electrochemical manner, but at a mercury electrode, there operated a CE mechanism.

Redox behaviour of transition metal complexes play an important part in catalytic reactions and *in vivo*. Electrochemical studies have offered valuable information on their reaction mechanisms [1]. We have investigated the preparation of a variety of transition metal isocyanide complexes by electrochemical methods. Recently we described how electrochemical reductions of platinum(II) and palladium(II) isocyanide complexes give bi- or/and tri-nuclear metal complexes containing metal–metal bonds [2,3]. Now, an extension has been made to a study of nickel(II) analogues. This paper contains an evaluation of the reductive behaviour of a complex *trans*-$NiI_2(RNC)_2$ ($R = 2,6\text{-}Me_2C_6H_3$); particularly notable was the dependence of the electrochemical response on electrode materials. Normal electrochemical behaviour of the complex was exhibited at the platinum electrode whereas at the mercury electrode the voltammetric response showed the preceding reaction (CE path) occurring. Similar electrode effects have been reported for a series of iron carbonyl complexes [4] and $CpM(CO)_2$ (M = Co, Rh) [5].

We report here the unusual dependence of the electrochemical reduction process on different electrodes and the isolation of the related complex.

Cyclic voltammograms (CVs) of *trans*-$NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1**) [6*] in a 0.1 *M* $MeCN/CH_2Cl_2$ (9 : 1) solution containing $[n\text{-}Bu_4N][ClO_4]$ as an electrolyte were measured at platinum tip and hanging-mercury-drop electrodes (Fig. 1). Voltammetry at a platinum-tip electrode showed a quasi-reversible redox wave near -0.5 V (vs. Fc/Fc^+) in addition to two irreversible oxidative waves at ca. $+0.2$ V (vs.

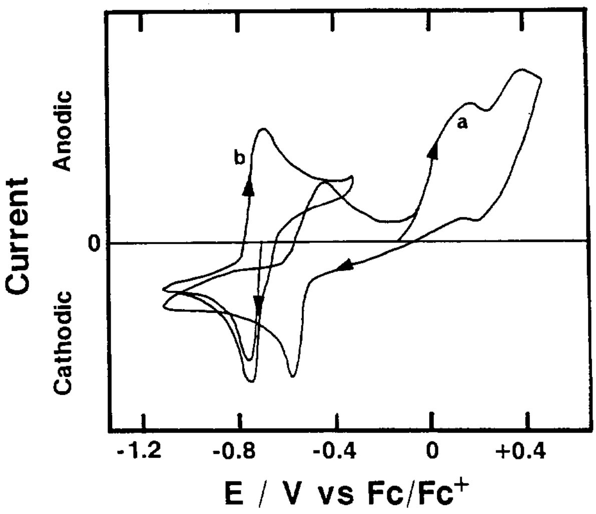

Fig. 1. Cyclic voltammograms of $NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1**) at Pt and Hg electrodes. (a) at Pt electrode; (b) at Hg electrode. Concentration: 1.0 m*M* solution (CH_2Cl_2/CH_3CN (1:9)/[n-Bu_4N][ClO_4]). Scan rate: 0.2 V/s.

Fc/Fc$^+$). For sweep rates (v) between 0.01 and 0.20 V/s, the ratio $i_p/v^{1/2}$ of the redox waves at −0.5 V was constant and $i_{pa}/i_{pc} = 1.0$, in accord with diffusion control. A potential separation between anodic and cathodic peaks was about 0.10 V for a sweep rate of 0.10 V/s, due to an ohmic drop with solution resistance. The coulometric electrolysis of **1** gave tetrakis(2,6-xylyl isocyanide)nickel(0) in a high yield [7*], suggesting that the redox reaction at −0.5 V proceeded with a two-electron transfer. Presence of two oxidative waves is out of accord with what would be expected of halide ion and was observed by the scan from −0.1 V (vs. Fc/Fc$^+$) to be associated with the anode. The conductivity of **1** is small enough for it to be considered as a non-electrolyte in acetonitrile. From these results, the two oxidative waves are assumed to be due to the complex **1**.

$$\begin{tikzcd}
NiI_2(2,6\text{-}Me_2C_6H_3NC)_2 \arrow[r, shift left, "+2e"] \arrow[d, "-e"] & {[NiI_2(2,6\text{-}Me_2C_6H_3NC)_2]^{2-}} \arrow[l, shift left, "-2e"] \\
{[NiI_2(2,6\text{-}Me_2C_6H_3NC)_2]^{+}} \arrow[r, "-e"] & {[NiI_2(2,6\text{-}Me_2C_6H_3NC)_2]^{2+}}
\end{tikzcd}$$

Voltammetry at a mercury electrode showed a redox couple at −0.69 V (vs. Fc/Fc$^+$) for a cathodic wave and at −0.79 V (vs. Fc/Fc$^+$) for an anodic wave (Fig. 1). This redox potential ($E_{1/2} = -0.74$ V) was lower by about 0.2 V than that measured at a platinum electrode. Differences of the voltammograms suggested formation of a new species on the surface of the mercury electrode.

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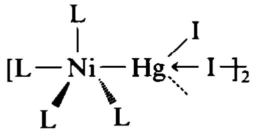
* Reference number with asterisk indicates a note in the list of references.

In an attempt to investigate the species, the reaction of **1** with mercury was carried out in the absence and the presence of 2,6-xylyl isocyanide. Both reactions gave orange air-stable crystals in high yields, formulated as $[Ni(RNC)_4HgI_2]$ ($R = 2,6\text{-}Me_2C_6H_3$) (**2**) [8*].



The CV of **2** at a platinum electrode showed a half-wave potential at −0.72 V, in good agreement with that measured at a mercury electrode. Differences according to electrode materials were not observed. The redox potential of **1** at a mercury electrode was inconsistent with that of **2**, but near the redox potential of **2**. It is known that the redox potentials for $NiI_2(RNC)_n$ ($n = 2$, 3) and $[Ni(RNC)_4]^+$ shifted to the positive side with increase of the number of isocyanide molecules [9*]. From these electrochemical behaviours, we can assume that a transient species such as "$Ni(RNC)_2HgI_2$" (**3**) has been formed initially by the chemical reaction before the electrochemical reaction occurs [10*]. In an attempt to examine the species, we

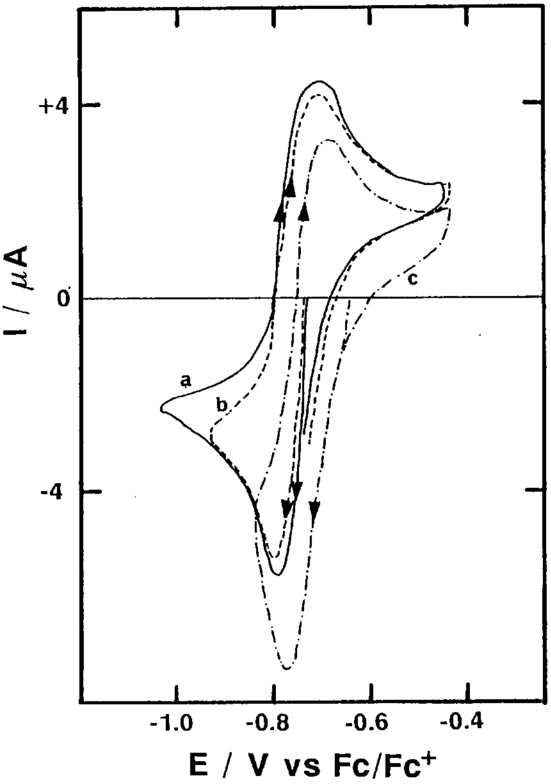
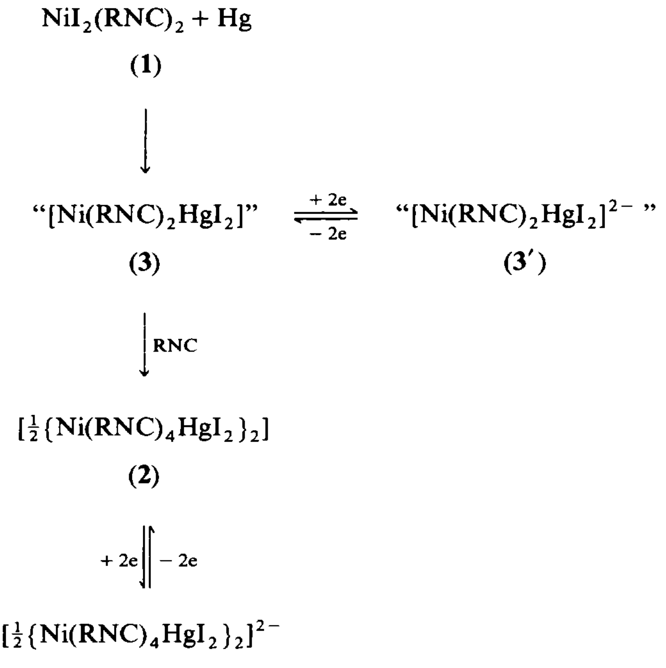


Fig. 2. Cyclic voltammograms of a mixture of $NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1**) and 2,6-xylyl isocyanide at Hg electrode in CH_2Cl_2/CH_3CN (1 : 9)/[n-Bu_4N][ClO_4]. (a) Ni complex **1**; (b) RNC/**1** = 1.4; (c) RNC/**1** = 4.0. Concentration of **1**: 0.6 m*M* solution. Scan rate: 0.2 V/s.



Scheme 1. Redox reactions of **1** and **2**.

measured the CVs of a mixture of **1** and 2,6-xylyl isocyanide. With increase of added isocyanide, the half-wave potential shifted, and finally the redox wave was in complete agreement with that of **2** (Fig. 2).

Since a macroscopic electrolysis of **2** gave $Ni(2,6\text{-}Me_2C_6H_3NC)_4$, an electroreduction of **3** is a two-electron transfer.

From these results, the reaction consists of an initial formation of a transient "$Ni(RNC)_2HgI_2$" species **3** from **1** and mercury. The species **3** was reduced electrochemically to produce **3′**. This reaction is reversible. In the presence of isocyanide, the species **3** captured isocyanide molecules to produce the Hg–Ni complex **2**, which led to a reversible two-electron redox reaction (Scheme 1).

Further studies are in progress.

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6 IR (KBr): 2136 cm^{-1} (N≡C). ^1H NMR ($CDCl_3$): δ 2.50 (s, Me), ca. 7.2 (m, aromatic protons). Anal. Found: C, 37.59; H, 3.25; N, 4.89. $C_{18}H_{18}N_2I_2Ni$ Calc.: C, 37.61; H, 3.16; N, 4.87%.

7 IR (nujol): 1995 cm^{-1} (N≡C). ^1H NMR (PhCl): δ 2.35 (s, Me). Anal. Found: C, 74.12; H, 6.27; N, 9.59. $C_{36}H_{36}N_4Ni$ Calc.: C, 74.11; H, 6.22; N, 9.60%.

8 IR (nujol): 2139, 2081 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.50 (s, Me), ca. 7.0 (aromatic protons). Anal. Found: C, 41.66; H, 3.50; N, 5.40. $C_{36}H_{36}N_4I_2HgNi$ Calc.: C, 41.60; H, 3.34; N, 5.40%. The structure of the complex of 4-bromo-2,6-dimethylphenyl isocyanide was confirmed by X-ray analysis. The configuration around a Ni atom is trigonal bipyramid, and that around a Hg atom distorted tetrahedral. Details will be reported elsewhere.

9 Half-wave potentials (vs. Fc/Fc^+) in $MeCN$-CH_2Cl_2 (8:1) at a platinum electrode: −0.52 V for $NiI_2(RNC)_2$, −0.488 V, $NiI_2(RNC)_3$ and −0.42 V, $[Ni(RNC)_4]^+$, respectively, where $R = 2,6$-$Me_2C_6H_3$.

10 The transient species **3** may be a structure such as "$Ni(RNC)_2(MeCN)_2HgI_2$", but there is no information at present.