Reduction of Carbon Dioxide by Nickel Macrocyclic Catalysts adsorbed on a Mercury Electrode or a Copper Rotating Disc Electrode

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A new method for evaluating the efficiency of nickel macrocyclic electrocatalysts for reduction of CO_2 to CO using a rotating copper disc electrode has led to the discovery of a new highly active complex, $[NiL^2]^{2+}$ [L^2 = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane (diazacyclam)].

The electrocatalytic reduction of the greenhouse gas CO_2 is gaining renewed interest.[1,2] Since the discovery that $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) electrocatalyses the selective reduction of CO_2 to CO when it is adsorbed onto mercury from aqueous solution,[3,4] studies have dealt in detail with the greater CO_2-binding affinity in dimethyl sulfoxide for cobalt and nickel complexes with lower M^{II}–M^{I} redox potentials,[5,6] but not the actual catalytic activity for the reduction of CO_2. Recently, a study of *N*-alkylated derivatives of $[Ni(cyclam)]^{2+}$ showed that the *N*-monomethylated cyclam was the best overall catalyst in terms of its reduction potential and stability, but gave lower catalytic currents than $[Ni(cyclam)]^{2+}$.[7] A dimeric cyclam complex was found to be less specific for CO_2 reduction and more active for the competing H_2 reduction reaction.[8] The nickel(II) complex of the peripherally methyl-substituted cyclam *C*-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane is apparently considerably less active than $[Ni(cyclam)]^{2+}$ under the same conditions (MeCN–H_2O) and gives more H_2 as byproduct.[9,†] A variety of unsaturated Schiff-base macrocycles have been studied[10,11] and we have recently shown that nickel(II) Schiff-base complexes are also active for the reduction of CO_2.[12]

In our search for a superior catalyst to $[Ni(cyclam)]^{2+}$ we required a saturated macrocyclic complex with a more positive metal-based reduction. In this communication we report the electrocatalysis of $[NiL^1][ClO_4]_2$[13] and $[NiL^2][ClO_4]_2$[14] {L^1 = 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1]eicosane, L^2 = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane (diazacyclam)}. Under an inert atmosphere these complexes have Ni^{II}–Ni^{I} reduction potentials in MeCN at −1.14 and −1.42 V *vs.* the saturated calomel electrode (SCE) respectively, compared to −1.45 V for $[Ni(cyclam)]^{2+}$ under the same conditions.

In the presence of CO_2 the Ni^{II}–Ni^{I} reduction wave of $[Ni(cyclam)]^{2+}$ in MeCN–H_2O (9:1 v/v) becomes irreversible and the cathodic current is greatly increased. Similarly for $[NiL^1]^{2+}$ there is an increase in cathodic current (i_{pc} = 25 μA at −1.34 V) and a small pre-wave (E_{pc} *ca.* −1.2 V) (Fig. 1). Under the same conditions but using $[Ni(cyclam)]^{2+}$ we have measured a catalytic current for CO_2 reduction of i_{pc} = 218 μA at −1.62 V. Although the catalytic current for $[NiL^1]^{2+}$ is much reduced compared to $[Ni(cyclam)]^{2+}$ the peak current is at a more positive potential by 280 mV.

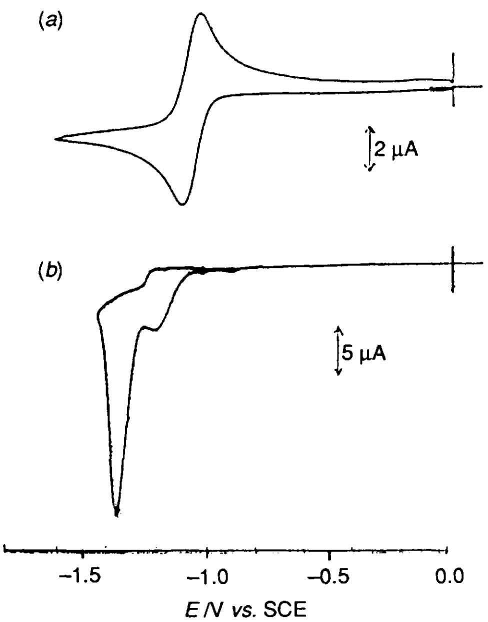
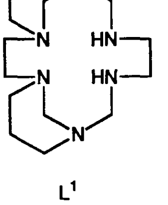
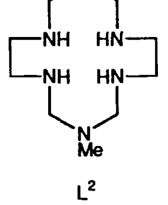


Fig. 1 Cyclic voltammetry (100 mV s^{-1}) of $[NiL^1]^{2+}$ at a hanging mercury drop electrode (area = 0.0139 cm^2) at 291 K in MeCN–H_2O (9:1)–0.1 mol dm^{-3} $NaClO_4$ under argon (*a*) and in a saturated solution of CO_2 (*b*)



L^1



L^2

The cyclic voltammogram of $[NiL^2][ClO_4]_2$ in MeCN–H_2O (9:1 v/v) displays a Ni^{II}–Ni^{I} redox couple at −1.44 V (ΔE = 120 mV) under argon but when carbon dioxide is bubbled through this solution there is a large catalytic current of 135 μA

[†] From Fig. 3 of ref. 9 we measure a catalytic current maximum of 2.68 mA cm^{-2} at a scan rate of 80 mV s^{-1}, compared to 9.35 mA cm^{-2} at 100 mV s^{-1} for $[Ni(cyclam)]^{2+}$. The use of mixed solvent is necessary in order to dissolve the complex.

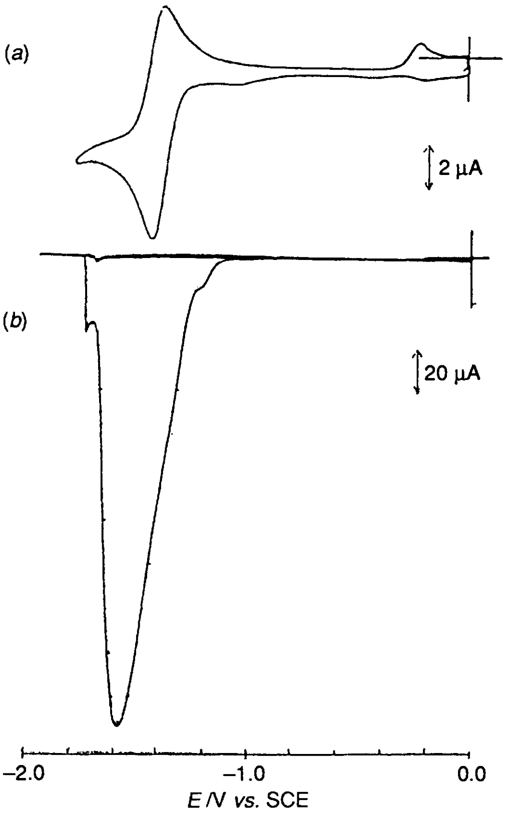


Fig. 2 Cyclic voltammetry (100 mV s^{-1}) of $[NiL^2]^{2+}$ at a hanging mercury drop electrode (area = 0.0139 cm^2) at 291 K in MeCN–H_2O (9:1)–0.1 mol dm^{-3} $NBu^n{}_4BF_4$ under argon (*a*) and in a saturated solution of CO_2 (*b*)

at −1.8 V (Fig. 2), with a pre-wave at −1.28 V, and an anodic peak appears at −0.18 V. The original voltammogram is restored only after prolonged degassing with argon to remove all traces of carbon dioxide. Repeating the experiment, we get the same catalytic current but a slightly different potential (−1.68 V). On allowing carbon dioxide to bubble for a longer period the current increases to a limiting value of 216 μA. Thus this complex is more active than $[Ni(cyclam)]^{2+}$ under the same conditions. Even though $[NiL^2][ClO_4]_2$ is essentially insoluble in water (solubility ≤ 1 mmol dm^{-3}) (so that the redox waves are not visible), bubbling carbon dioxide into a 0.5 mmol dm^{-3} aqueous solution of $[NiL^2]^{2+}$ yields a catalytic current of 45 μA at −1.4 V.

From the scan-rate dependence of the catalytic current (v = 10–100 mV s^{-1}) for the $[NiL^2]^{2+}$–CO_2 system we can plot the shift in the E_{pc} values against log (v/mV s^{-1}). If we assume that the catalyst is situated on the electrode then the theory for a totally irreversible redox system is applicable.[15,*] Thus, $i_{p,cat}$ is proportional to both carbon dioxide concentration and $v^{\frac{1}{2}}$ and E_{pc} shifts cathodically by $30/\alpha n$ mV per ten-fold increase in scan rate at 25 °C, where α is the transfer coefficient and n is the number of electrons transferred in the rate-determining step. A high value of 159 mV is observed, consistent with the low value of α (0.27) observed for the reduction of CO_2 at a bare mercury electrode in dimethylformamide,[16] which was shown to be a one-electron process [equation (1)].

$$CO_2 + H_2O + e^- \longrightarrow HCO_2(ads) + OH^- \quad (1)$$

Similar values of the slope were obtained for $[NiL^1]^{2+}$ and $[Ni(cyclam)]^{2+}$ under the same conditions. The high value of the slope may also be related to resistance effects arising in the solvent [MeCN–H_2O (9:1 v/v)] at these high catalytic currents.

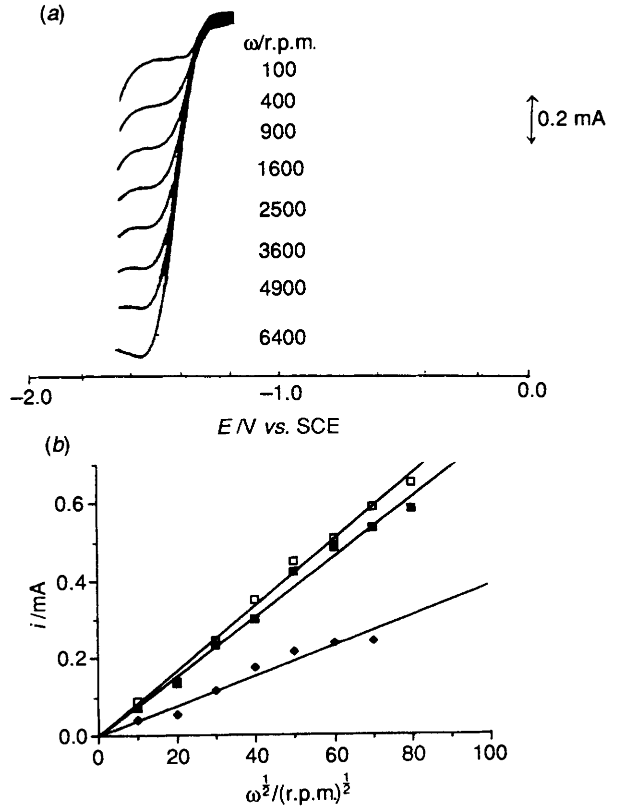


Fig. 3 (*a*) Current–voltage curves for a copper rotating disc (area 0.071 cm^2) with adsorbed $[Ni(cyclam)]^{2+}$ in MeCN–H_2O (9:1)–0.1 mol dm^{-3} $NaClO_4$ saturated with CO_2 at 288 K (scan rate = 20 mV s^{-1}) and (*b*) corresponding Levich plots for the three complexes investigated after correction for background hydrogen evolution; $[Ni(cyclam)]^{2+}$ (□), $[NiL^1]^{2+}$ (◆), $[NiL^2]^{2+}$ (■)

We then studied the catalysis under steady-state conditions at a rotating disc electrode. Initial rotating disc electrode experiments were attempted using mercury-plated glassy carbon or copper working electrodes, however stable steady-state waves could not be observed due to the interference from evolution of H_2. Instead we found that bare copper itself was a suitable substrate. Some problems with reproducibility of the data were encountered, and this was traced to inadvertant corrosion of the copper disc in MeCN. Rotating disc electrode current–voltage curves are shown in Fig. 3(*a*) for the $[Ni(cyclam)]^{2+}$ catalysed reduction of CO_2, and the corresponding Levich curves, i *vs.* $\omega^{\frac{1}{2}}$ where ω is the rotation rate in revolutions per minute (r.p.m.), for this complex are compared with those for $[NiL^1]^{2+}$ and $[NiL^2]^{2+}$ in Fig. 3(*b*). The slopes of the Levich plots indicate that the reduction of CO_2 is a two-electron process for the $[Ni(cyclam)]^{2+}$ and $[NiL^2]^{2+}$ catalysts, using appropriate values[1] for the diffusion coefficient of CO_2 (10^{-6} cm^2 s^{-1}), its solubility (0.040 mol dm^{-3}) and the area of the electrode (0.071 cm^2). The slope of the Levich plot for $[NiL^1]^{2+}$ is half this value suggesting that this reduction is a one-electron process. The intercepts of the Koutecky–Levich curves (i^{-1} *vs.* $\omega^{-\frac{1}{2}}$) are very small and difficult to determine with great precision due to the scatter of the data; however we find that all of the catalysts have kinetic currents greater than 5 μA.

The results for $[Ni(cyclam)]^{2+}$ and $[NiL^2]^{2+}$ are consistent with the mechanism proposed by Sauvage and co-workers,[3,4] which has recently been probed by *ab initio* calculations.[17] We propose that the good catalytic activity of the diazacyclam complex may be due to hydrogen-bonding interactions between co-ordinated CO_2 and the remote tertiary amine group, as proposed for co-ordinated Cl and H_2O in the related 3-methyl-

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[*] It should be pointed out that a small correction should be made for the spherical nature of the electrode.[15b]

1,3,5,8,12-pentaazacyclotetradecane (azacyclam) complex.[18] On the other hand, the diazacyclam L^2 is known to stabilise the high-spin state by stabilisation of the axial ligands.

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