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The preparation, chemistry and crystal structure of the nickel(II) complex of N-hydroxyethylazacyclam [3-(2′-hydroxyethyl)-1,3,5,8,12-penta-azacyclotetradecane nickel(II) perchlorate]. A new electrocatalyst for CO_2 reduction

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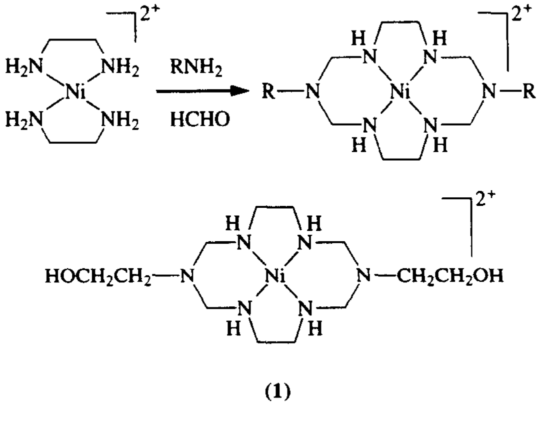
Abstract—The reaction of formaldehyde and ethanolamine with the nickel(II) complex of 1,9-diamino-3,7-diazanonane (2,3,2-tet) gives the nickel(II) complex of the macrocycle 3-hydroxyethyl-1,3,5,8,12-penta-azacyclotetradecane (L) which can be readily isolated as the perchlorate salt. The crystal structure of $[NiL](ClO_4)_2$ has been determined. The nickel atom is in an essentially planar environment with N_1, N_5, N_8 and N_{12} acting as donors with Ni—N bond distances in the range 1.930–1.938 Å The ligand has a trans III configuration of the *sec*-NH centres with chair six-membered and gauche five-membered chelate rings. The hydroxyethyl group on N_3 is axial. The two perchlorate anions lie in the axial sites but the Ni—O(4) and the Ni—O(7) distances of 2.836(3) and 3.028(3) Å indicate that there is no bonding interaction between these centres. In aqueous solution the complex is predominantly square planar. Addition of HCl leads to axial addition of chloride while addition of thiocyanate gives the *trans*-$[NiL(NCS)_2]$ complex. The ligand readily folds to give *cis*-complexes. Thus addition of ethylenediamine to $[NiL]^{2+}$ gives *cis*-$[NiL(en)]^{2+}$ in solution. The electrochemistry of $[NiL]^{2+}$ has been studied in detail. The complex is a good electrocatalyst for the reduction of CO_2. The complex was less active for hydrogen evolution in an acetate electrolyte than $[Ni(cyclam)]^{2+}$ and thus appeared to be more active than the cyclam complex for CO_2 reduction under these conditions. © 1997 Elsevier Science Ltd

Keywords: macrocycle; nickel complex; electrocatalyst; CO_2 reduction.

In a previous paper we have discussed the preparation and general chemistry of the nickel(II) complex of the pendant arm macrocycle (1) prepared by the reactions outlined in Scheme 1 [1]. These complexes are examples of 'padlock' macrocycles [2] in which ring closure is brought about by the addition of various padlocking nucleophiles such as RNH_2, $[CH_3CHNO_2]^-$ and $[CH(CO_2Et)_2]^-$ to the tetra-imine produced by the reaction of formaldehyde with the nickel(II) complex shown in Scheme 2. The reaction can be regarded as a special type of Michael addition reaction as the imine bond is quite highly polarised by the metal ion



(1)

Scheme 1.

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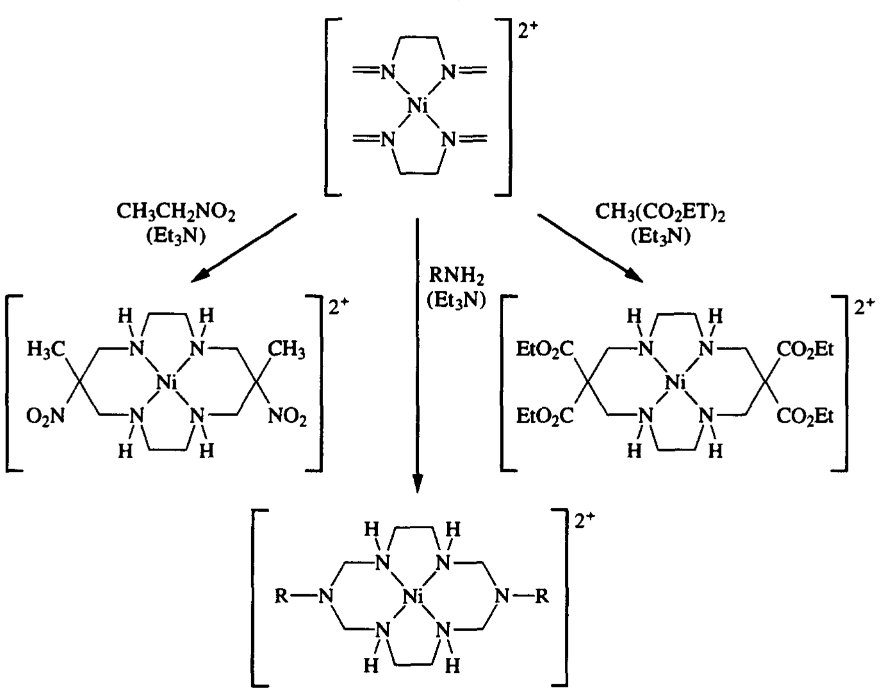
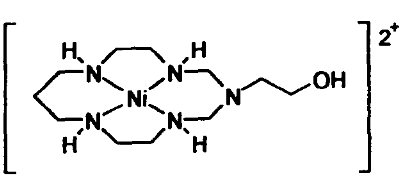


Scheme 2.

which acts as a Lewis acid. A range of possible nucleophiles can be used leading to novel pendant arm derivatives. A Spanish group [3] have found that (**1**) reacts with LiTCNQ to give [NiL(TCNQ)$_2$] and have determined the crystal structure of the compound which is of interest in the materials field (TNCQ = 7,7,8,8-tetracyano-p-quinodimethane).

In the present paper we discuss the reaction of HCHO and $H_2NCH_2CH_2OH$ with the nickel(II) complex of the tetramine 1,9-diamino-3,7-diazanonane (2,3,2-tet) to give the nickel(II) complex (2 = [NiL]$^{2+}$). We have also determined the crystal structure of the complex and studied its chemistry and electrochemistry in detail.



(2 = [NiL]$^{2+}$)

EXPERIMENTAL

1,9-Diamino-3,7-diazanonane was prepared as described by Barefield *et al.* [4] and purified by vacuum distillation.

[NiL](ClO$_4$)$_2$

To a solution of $NiCl_2 \cdot 6H_2O$ (5.75 g) in ethanol (120 cm^3) was added dropwise 1,9-diamino-3,7-diazanonane (2,3,2-tet) (3.87 g). A violet solution resulted to which triethylamine (4.8 g), aqueous ethanolamine (8.5 cm^3, 40%) and formaldehyde (11 cm^3, 36%) were slowly added. The solution was refluxed for 24 h after which time the precipitate of Ni(OH)$_2$ was removed by filtration. A saturated solution of sodium perchlorate was added to the filtrate which on refrigeration gave orange crystals, which were filtered off and recrystallised from water–ethanol and then dried *in vacuo* over silica gel. Found: C, 26.2; H, 5.3; N, 13.7. Calc. for $C_{11}H_{27}N_5NiCl_2O_9$: C, 26.3; H, 5.4; N, 13.9%. A 1×10^{-3} mol dm^{-3} solution of the complex in water gave $\Lambda_M = 237$ S cm^{-2} mol^{-1} consistent with a 2 : 1 electrolyte.

The thiocyanate derivative *trans*-[NiL(NCS)$_2$] was readily prepared as follows. To a solution of [NiL](ClO$_4$)$_2$ (0.44 g, 1.87 mmol) in water (25 cm^3) was added a saturated aqueous solution of KNCS (5 cm^3) dropwise with stirring. The pale pink lilac complex precipitated almost immediately from solution and was filtered off, washed with water and dried *in vacuo*. The complex can be recrystallised from MeNO$_2$. Found: C, 37.4; H, 6.35; N, 23.5. Calc. for $C_{13}H_{27}N_7ONiS_2$: C, 37.2; H, 6.5; N, 23.35%.

The complex *cis*-[NiL(en)]$^{2+}$ was pepared in solution by the dropwise addition of 1,2-diaminoethane to a concentrated solution of [NiL](ClO$_4$)$_2$.

Measurements

Visible spectra were determined with a Perkin–Elmer Lambda 14 spectrophotometer. Infrared spectra were measured using KBr discs on a Perkin–Elmer FT instrument. Conductivities were measured with an AGB 100 conductivity meter.

Crystal structure determination of $[NiL](ClO_4)_2$

A suitable crystal was obtained by slow recrystallisation from ethanol–water. Measurements were made at 25°C with a Rigaku AFC7S diffractometer with graphite monochromated Mo—K_α radiation ($\lambda = 0.71069$ Å). The crystal data and other experimental parameters are summarised in Table 1. The intensities were corrected for Lorentz, polarisation and absorption effects. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.82 to 1.00.

Structure solution and refinement

The structure was solved by direct methods [11] and expanded by Fourier techniques [12]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically and the rest were included in fixed positions. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.53 and -0.40 e Å^{-3}, respectively. Selected bond distances and bond angles are summarised in Table 2.

Electrochemistry

Cyclic voltammetry was carried out using an EG and G PARC 273 A Potentiostat/Galvanostat controlled by version 4.11 of the Electrochemistry Research software package running on a PC. The cell used a saturated calomel electrode (SCE) as reference with a Luggin capillary and a Pt wire as counter (auxiliary) electrode. The working electrode was either Pt wire sealed in glass (0.5 mm diameter, 0.00196 cm^2) a hanging mercury drop electrode (Metrohm, 0.0087 cm^2 area) or a glassy carbon electrode (BAS, catalogue number MF-2012, 0.0707 cm^2). No IR compensation was used for CV's in acetonitrile, under the same conditions a peak separation of 75 mV was observed for ferrocene. The water employed was triply distilled and the $KHCO_3$ and sodium acetate electrolytes for aqueous solution studies were AR grade (Fisher). The acetonitrile (Aldrich HPLC grade) was distilled from P_2O_5 and solutions were 0.1 mol dm^{-3} in tetra-*n*-butylammonium hexafluorophosphate (Fluka, electrochemical grade).

Table 1. Crystal data for $[NiL](ClO_4)_2$

Formula weight	$C_{11}H_{27}N_5O_9Cl_2Ni$/502.97
Colour and habit	orange/block
Crystal system	primitive monoclinic
Systematic absences	h0l : $h+l = 2n$
	0k0 : $k = 2n$
Space group	$P2_1/n$ (No. 14)
a (Å)	9.598(4)
b (Å)	13.688(3)
c (Å)	14.830(3)
β (°)	94.60(2)
V (Å^3)	1942.1(9)
Z	4
D_c (g cm^{-3})	1.72
μ (Mo-K_α) (cm^{-1})	13.3
$F(000)$	1048
Scan method	ω–2θ
Max. 2θ (°)	50
Crystal size (mm)	$0.40 \times 0.20 \times 0.15$
Scan rate (° min^{-1})	16
No. of observed reflections ($I > 3\sigma(I)$)	2824
R	0.037
R_w	0.033
GOF	2.88

RESULTS AND DISCUSSION

The reaction of formaldehyde and ethanolamine with the nickel(II) complex of 1,9-diamino-3,7-diazanoname (2,3,2-tet) in the presence of the weakly coordinating base triethylamine gives the nickel(II) complex of the macrocycle 3-hydroxyethyl-1,3,5,8,12-penta-azacyclotetradecane $[NiL]^{2+}$ which can be readily isolated as the planar orange perchlorate salt. In nitromethane solution the complex has λ_{max} 460 nm ($\varepsilon = 60$ dm^3 mol^{-1} cm^{-1}). In aqueous solution there is evidence for a square planar $\rightleftharpoons$ octahedral equilibrium $[NiL]^{2+} + 2H_2O \rightleftharpoons [NiL(OH_2)_2]^{2+}$. The ^1H NMR spectrum in $MeNO_2$ is quite sharp as expected for a diamagnetic planar d^8 complex. Addition of one drop of D_2O to the solution leads to pronounced paramagnetic line broadening as axial addition gives the paramagnetic octahedral complex (Fig. 1). Addition of concentrated hydrochloric acid to an aqueous solution of the complex gives the blue–violet dichloro-complex in solution, while addition of potassium thiocyanate gives *trans*-$[NiL(NCS)_2]$ which can be readily isolated. Addition of 1,2-diaminoethane to an aqueous solution of $[NiL]^{2+}$ gives the folded *cis*-$[NiL(en)]^{2+}$ with a typical octahedral spectrum (Fig. 2) establishing that macrocycles of this type readily fold in the presence of chelating ligands.

The bridgehead nitrogen carrying the hydroxethyl substituent is much less basic than would be expected for a normal tertiary amino group which usually has a pK value of *ca* 9. The low basicity presumably arises due to electrostatic effects which make it difficult to protonate a dication of this type. Previous studies of the N—Me complex [5] have indicated that the pK of this nitrogen is less than 2.

Crystal structure of $[NiL](ClO_4)_2$

Crystals suitable for X-ray diffraction studies were obtained by slow recrystallisation from ethanol–water solution. An ORTEP view of the molecule with the atomic numbering system is shown in Fig. 3. Selected

Table 2. Selected bond distances (Å) and angles (°)

Ni(1)—N(2)	1.934(3)	Ni(1)—N(3)	1.938(3)
Ni(1)—N(4)	1.937(3)	Ni(1)—N(5)	1.930(3)
O(1)—C(11)	1.422(5)	N(1)—C(1)	1.427(5)
N(1)—C(9)	1.426(5)	N(1)—C(10)	1.475(4)
N(2)—C(1)	1.503(4)	N(2)—C(2)	1.494(4)
N(3)—C(3)	1.486(5)	N(3)—C(4)	1.498(5)
N(4)—C(6)	1.470(5)	N(4)—C(7)	1.488(5)
N(5)—C(8)	1.498(4)	N(5)—C(9)	1.503(4)
C(2)—C(3)	1.498(6)	C(4)—C(5)	1.505(6)
C(5)—C(6)	1.509(6)	C(7)—C(8)	1.485(6)
C(10)—C(11)	1.492(5)		

N(2)—Ni(1)—N(3)	87.0(1)	N(2)—Ni(1)—N(4)	178.5(1)
N(2)—Ni(1)—N(5)	92.1(1)	N(3)—Ni(1)—N(4)	94.2(1)
N(3)—Ni(1)—N(5)	179.1(1)	N(4)—Ni(1)—N(5)	86.7(1)
C(1)—N(1)—C(9)	114.5(3)	C(1)—N(1)—C(10)	116.6(3)
C(9)—N(1)—C(10)	115.9(3)	Ni(1)—N(2)—C(1)	118.1(2)
Ni(1)—N(2)—C(2)	108.4(2)	C(1)—N(2)—C(2)	110.0(3)
Ni(1)—N(3)—C(3)	107.9(2)	Ni(1)—N(3)—C(4)	119.4(3)
C(3)—N(3)—C(4)	109.7(3)	Ni(1)—N(4)—C(6)	119.1(2)
Ni(1)—N(4)—C(7)	107.7(2)	C(6)—N(4)—C(7)	110.1(3)
Ni(1)—N(5)—C(8)	108.5(2)	Ni(1)—N(5)—C(9)	117.5(2)
C(8)—N(5)—C(9)	110.0(3)	N(1)—C(1)—N(2)	113.8(3)
N(2)—C(2)—C(3)	106.3(3)	N(3)—C(3)—C(2)	106.7(3)
N(3)—C(4)—C(5)	111.7(3)	C(4)—C(5)—C(6)	112.6(4)
N(4)—C(6)—C(5)	112.2(3)	N(4)—C(7)—C(8)	106.6(3)
N(5)—C(8)—C(7)	105.7(3)	N(1)—C(9)—N(5)	113.3(3)
N(1)—C(10)—C(11)	112.4(3)	O(1)—C(11)—C(10)	108.7(4)

bond distances and bond angles are summarised in Table 2. The nickel atom is in a planar environment with N(2), N(3), N(4) and N(5) acting as donors with Ni—N bond distances in the range 1.930–1.938 Å which is quite normal for a low spin planar nickel(II) complex. The hydroxyethyl side arm on N(1) does not interact with the central nickel atom. A more detailed view of the ligand stereochemistry is given in Fig. 4. The ligand has a trans III configuration of the *sec*-NH centres which is the most thermodynamically fav-

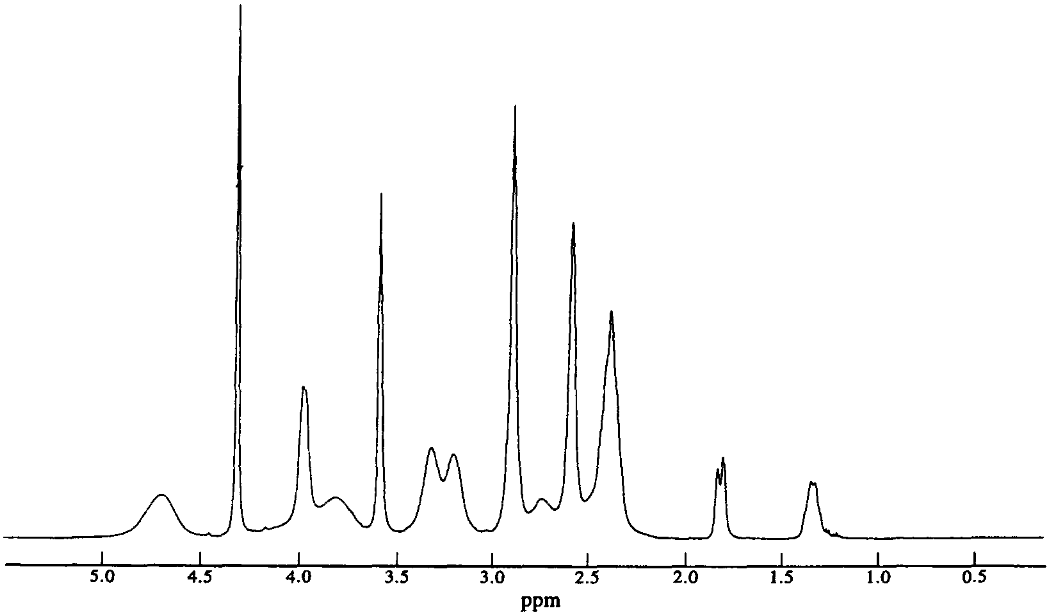


Fig. 1. ^{1}H NMR spectrum of $[NiL](ClO_4)_2$ in nitromethane after addition of one drop of D_2O showing paramagnetic line broadening.

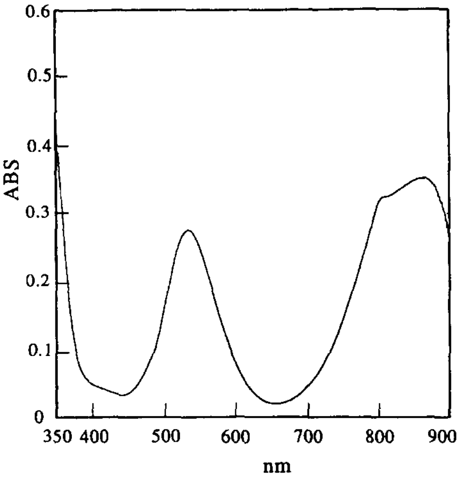


Fig. 2. The UV–vis spectrum of [NiL(en)]$^{2+}$ in aqueous solution. The absorption maxima are 536 nm (ε = 7) and 887 nm (ε = 10 dm^3 mol^{-1} cm^{-1}).

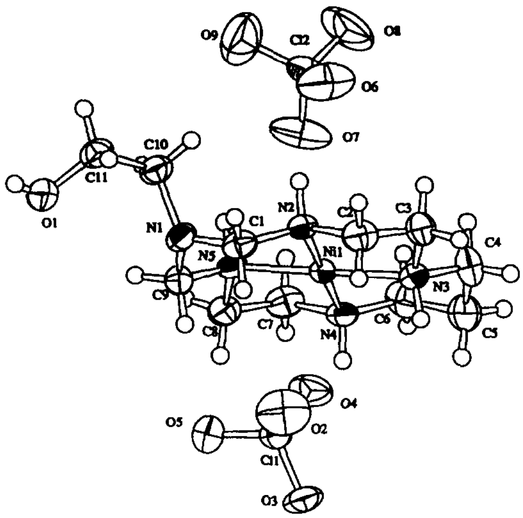


Fig. 3. Crystal structure of [NiL](ClO$_4$)$_2$ with the atomic numbering scheme.

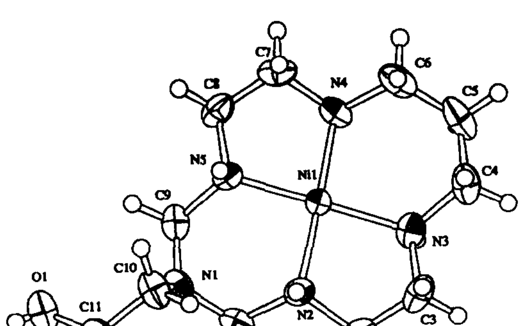


Fig. 4. View of the ligand conformation in the crystal structure.

oured configuration of the 1,4,8,11-tetra-azacyclotetradecane (cyclam) ring system leading to chair six-membered rings and gauche five-membered rings. The hydroxyethyl substituent on N(1) is axial and a similar stereochemistry has been observed in the N—Me and N—Et derivatives with nickel(II). The two perchlorate anions lie in the axial sites with Ni—O bond distances of 2.836(3) and 3.028(3) A indicating that there is no interaction between O(4) and O(7) and the central nickel atom in the solid state. Ballester and coworkers [3] have recently determined the crystal structure of [NiL$_{I}$](TCNQ)$_2$] (TCNQ = 7,7,8,8-tetracyano-p-quinodimethane) where NiL$_{I}$ = (**1**). This complex is octahedral with Ni—N bond distances of 2.053(4) and 2.056(5) Å typical for octahedral nickel (II) complexes. As found with the present structure the complex has a *trans* III arrangement of the *sec*-NH centres. The nickel atom is located at a centre of inversion with the hydroxyethyl groups in axial sites. The compound can be seen in parallel chains made up of [Ni(macrocycle)]$^{2+}$ units held together by the dimeric (TCNQ)$_2^{2-}$.

Electrochemistry

The electrochemistry of the complex [NiL]$^{2+}$ was studied to compare its activity with that of [Ni(cyclam)]$^{2+}$ in the electrocatalytic reduction of CO$_2$ to CO. The latter complex is a well known catalyst for this reaction. The Ni^{III}/Ni^{II} and Ni^{II}/Ni^{I} redox processes were studied in acetonitrile as solvent prior to the electrocatalysis measurements. Cyclic voltammetric measurements are summarised in Table 3. Both complexes display Ni^{III}/Ni^{II} waves close to +1.0 V. The Ni^{II}/Ni^{I} couple for [NiL]$^{2+}$ occurs at −1.416 V on carbon similar to that of [Ni(cyclam)]$^{2+}$ on Pt. However, the reduction behaviour of both complexes depended strongly on the type of electrode employed, indicating the occurrence of adsorption effects. Both complexes showed an additional broad cathodic wave at −0.7 to −0.8 V which appeared to be associated with adsorption of the complex and caused broadening, splitting and shifts of the Ni^{II}/Ni^{I} waves at solid electrodes. These effects were greatest for [Ni(cyclam)]$^{2+}$ on carbon and were removed when 1 mmol dm^{-3} water was present leading to a positive shift in the Ni^{II}/Ni^{I} redox potential.

In aqueous media under argon the cyclic voltammetry of the complexes at a hanging drop mercury electrode showed broad waves for the Ni^{II}/Ni^{I} reduction which were comparable in potential (Table 4 and the solid lines of Fig. 5). On the return scan there is a small sharp peak at *ca* −0.2 V which has previously been assigned to a carbonyl adduct of the nickel complexes. This result suggests that there is some residual CO$_2$ in carbonate media even in the absence of externally introduced CO$_2$. When CO$_2$ is bubbled into the bicarbonate buffer solution (Fig. 5, dashed lines) the catalytic current measured with

Table 3. Electrochemical data for the complexes $[NiL]^{2+}$ and $[Ni(cyclam)]^{2+}$ in acetonitrile with 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte

		Ni^{III}/Ni^{II}		Ni^{II}/Ni^{I}	
Complex	Electrode	$E_{1/2}{}^{a}$ (V)	ΔE_p (mV)	$E_{1/2}$ (V)	ΔE_p (mV)
$[NiL](ClO_4)_2$	Pt	+1.013	82	-1.536^{b}	184^{b}
	C	+1.000	92	−1.416	84
	Hg	—	—	−1.541	502
$[Ni(cyclam)](ClO_4)_2$	Pt	+1.032	96	−1.420	108
	C	+0.993	98	−1.644	172

[a] $E_{1/2} = (E_p^a + E_p^c)/2$.

[b] Ni^{II}/Ni^{I} has prewave at −1.38 V.

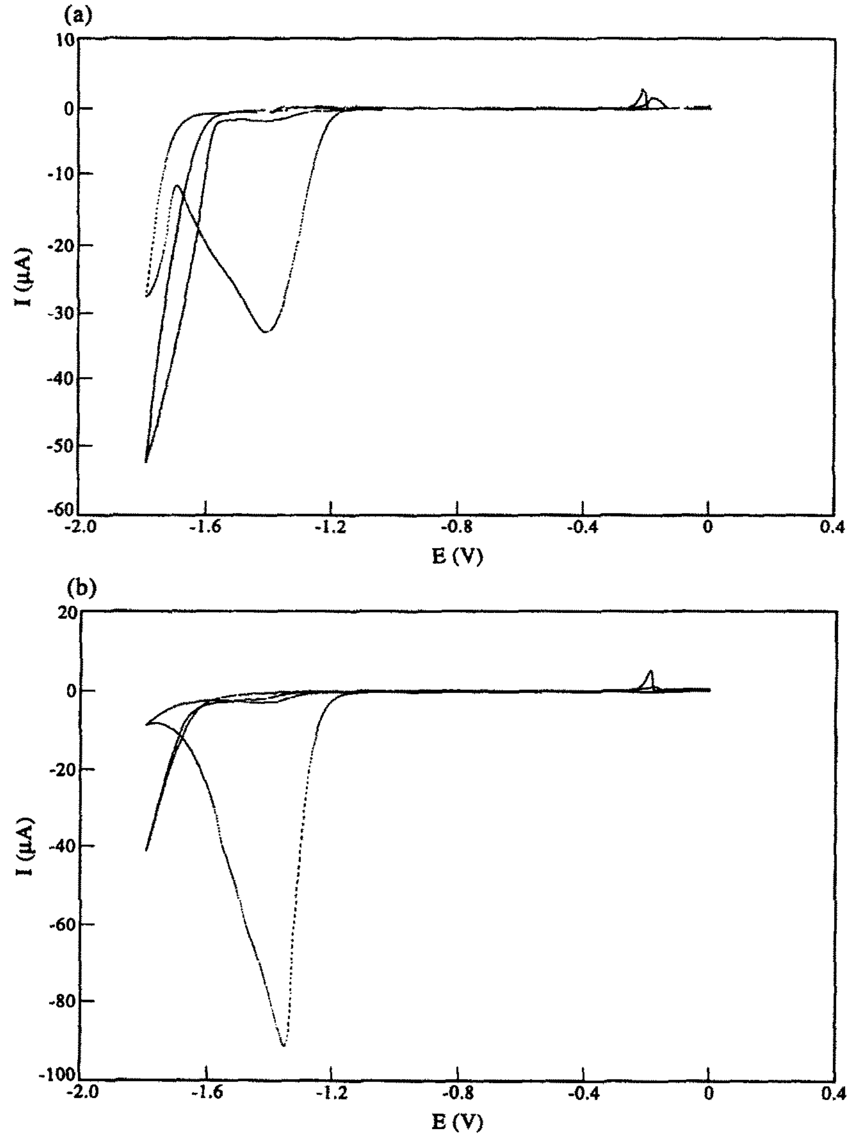


Fig. 5. Cyclic voltammograms (100 mV s^{-1}, SCE reference electrode) at a hanging mercury drop (area = 0.0087 cm^2) in 0.1 mol dm^{-3} $KHCO_3$, (—) under argon, (---) under CO_2 for (a) 1×10^{-3} mol dm^{-3} $[NiL](ClO_4)_2$ and (b) 1×10^{-3} mol dm^{-3} $[Ni(cyclam)](ClO_4)_2$. Note the different current scales for the two complexes.

Table 4. Electrochemical data for the electrocatalytic reduction of CO_2 in aqueous media

Complex	Electrolyte	$E_{1/2}(Ni^{II/I})^a$ (V)	ΔE_p (mV)	E_p^c (V)	i_p^c (μA)
$[NiL](ClO_4)_2$	0.1 M $KHCO_3$	-1.4^b	—	-1.41	33
	0.1 M NaOAc	-1.53	60	-1.46	62
[Ni(cyclam)]	0.1 M $KHCO_3$	-1.4	—	-1.36	92
	0.1 M NaOAc	-1.43^c	60	-1.80	30

[a] $E_{1/2} = (E_p^a + E_p^c)/2$.

[b] The CO_2 concentration was ca. 0.032 mol dm^{-3}. The 0.1 mol dm^{-3} solution of $KHCO_3$ had a pH = 6.2–6.8 and the 0.1 mol dm^{-3} solution of NaOAc had a pH = 7.38 which fell to 5.8 after bubbling with CO_2.

[c] Estimated : cathode peak obscured by hydrogen evolution current.

$[NiL]^{2+}$ is about 1/3 of that of the cyclam complex under the same conditions. The cathodic peak was also 50 mV more positive. Clearly the present complex does not give as much catalytic current under cyclic voltammetric conditions as $[Ni(cyclam)]^{2+}$ or the dialkyldiazacyclam nickel complex previously reported.

It is noteworthy that the data indicate that $[NiL]^{2+}$ is less active for hydrogen evolution in an acetate electrolyte than the cyclam complex and thus appeared to be more active than the cyclam complex for CO_2 reduction under these conditions. A further observation is that prolonged CO_2 bubbling in 0.1 mol dm^{-3} $KHCO_3$ leads to loss of the catalytic current for $[Ni(cyclam)]^{2+}$ and decolourisation of the solution. The complex $[NiL]^{2+}$ is more resistant to this effect. The visible spectra of the decolourised solutions are consistent with the formation of a carbonate adduct and is being further investigated.

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