Stabilization of Monovalent Nickel in Aqueous Solutions by a Saturated Tetra-aza-macrocyclic Ligand

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The planar form of the complex *C-meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetra-azacyclotetradecanenickel(I) $\{[Ni(L^1)]^+\}$ is shown to be stable in aqueous solutions, with $t_{\frac{1}{2}} > 100$ h and the formal potential of the couple $[Ni(L^1)]^{2+}/[Ni(L^1)]^+$ is −0.98 V *vs.* standard calomel electrode; redox reactions involving this couple were studied and compared with those of the couple $[Ni(L^2)]^{2+}/[Ni(L^2)]^+$ (L^2 = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane).

Many nickel(I) complexes with tetra-aza-macrocyclic ligands have been prepared in aprotic media,[1] which are unstable in aqueous solution.[2] The mechanism of their reactions with water was not reported but mechanisms A and B seem plausible. In mechanism A, reaction (1)[2] is followed by reaction (2), or by hydride transfer to the ligand if the latter is unsaturated. No report on hydrogen formation in the decomposition of LNi^{I} is known to us, although LNi^{II} complexes have been shown to be electrocatalysts for hydrogen production.[3a–c] In the alternative mechanism B, the monovalent nickel complexes might lose their ligand *via* reaction (3),

$$\mathrm{LNi^{I} + H_2O{-}H_3O^+ \rightarrow LNi^{III}{-}H + OH^-{-}H_2O} \quad (1)$$

$$\mathrm{LNi^{III}{-}H + H_2O{-}H_3O^+ \rightarrow LNi^{III} + H_2 + OH^-{-}H_2O} \quad (2)$$

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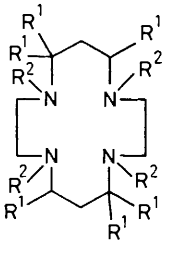
† Deceased, August 5th, 1981.



cyclam, $R^1 = R^2 = H$
L^1, $R^1 = R^2 = Me$
L^2, $R^1 = Me$, $R^2 = H$ } *C-meso*-isomers

by analogy with processes observed for monovalent copper complexes.[3d]

$$LNi^I + nH_2O\text{–}nH_3O^+ \rightarrow Ni^+_{aq} + LH_n^{n+} + nOH^-\text{–}nH_2O \quad (3)$$

It was recently shown that the planar form of the nickel(II) complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane [formed by methylation of Ni^{II}(cyclam)] is substitution-inert,[4] whereas isomeric pentaco-ordinated complexes are formed by reactions of the permethylated ligand with divalent cations.[5] We have studied the redox properties of the planar form of *C-meso*-1,4,5,7,7,8,11,12,-14,14-decamethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II) $[Ni(L^1)][ClO_4]_2$ in aqueous solutions as we hoped that the methyl substituents on the nitrogen atoms would inhibit reaction (3).

The complex $[Ni(L^1)][ClO_4]_2$ was synthesized by methylation of the complex $[Ni(L^2)][ClO_4]_2$ with MeI[4b] and recrystallized from triply distilled water. The i.r. spectrum (KBr) showed no N–H stretching absorption and the n.m.r. spectrum was in good agreement with that reported by Barefield.[4a]

$[Ni(L^1)]^{2+}$ is polarographically reduced in aqueous solutions at pH 7.0 or 11.5 in a quasi-reversible single-electron process with a half-wave potential of −1.05 V *vs.* S.C.E. (standard calomel electrode), independent of the nature of the supporting electrolyte NaCl, $NaClO_4$, or Me_4NCl. In all cases a small prewave presumably due to adsorption was observed. Similar results were observed in cyclic voltammetric experiments with a hanging mercury drop electrode, indicating that $[Ni(L^1)]^+$ is relatively stable (Figure 1).

Preparative electrolysis was carried out with a mercury pool as a working electrode at −1.2 V *vs.* S.C.E. {solution composition 3×10^{-4} M-$[Ni(L^1)][ClO_4]_2$, 0.1 M-Me_4NCl, pH 7.0}. Coulometric calculations proved the one-electron nature of the reduction process. The product has an absorption band with λ_{max} 335 ± 2 nm and ϵ_{max} 3600 ± 500 dm^3 mol^{-1} cm^{-1}. After 18 h the absorption at 335 nm had decreased by <10% indicating $t_{\frac{1}{2}}$ $\{[Ni(L^1)]^+\} > 100$ h under these conditions.‡ Thus the results demonstrate that $[Ni(L^1)]^+$ is considerably more stable than the planar form of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecanenickel(I), which decomposes even in tetrahydrofuran by a relatively fast second-order process,[6] or $[Ni(L^2)]^+$.§[2] Polarograms measured in completely reduced solutions show a one-electron oxidation wave close to the $[Ni^{II}(L^1)]$ reduction wave; analysis during the electrolysis gives a common oxidation–reduction polarographic wave. Bubbling oxygen through the reduced solution resulted in the back formation of $[Ni^{II}(L^1)]$. Acidifying the solution to pH 1.0 with HCl caused decomposition of $[Ni(L^1)]^+$ whereas the use of $HClO_4$ precipitated a white compound which is stable in the absence of air.

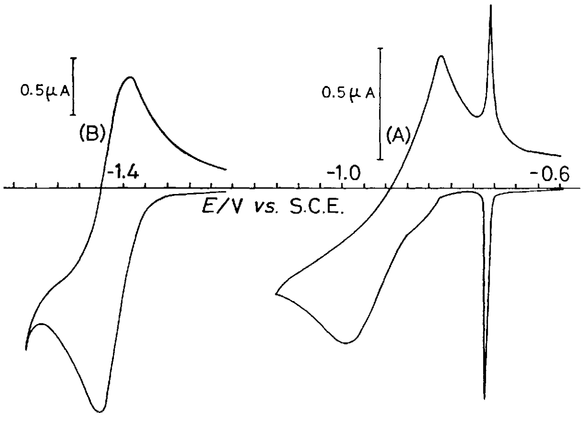


Figure 1. Cyclic voltammograms at a hanging mercury drop electrode at pH 7.0; supporting electrolyte 0.1 M Me_4NCl; scan rate 50 mV s^{-1}. The voltammogram for (A) was measured directly after the formation of the drop.** (A) 3×10^{-4} M-$[Ni(L^1)][ClO_4]_2$; (B) 1×10^{-3} M-$[Ni(L^2)][ClO_4]_2$.

It is of interest that the cyclic voltammogram of $[Ni(L^1)]^{2+}$ (Figure 1) suggests a formal potential of −0.98 V *vs.* S.C.E. for the couple $[Ni(L^1)]^{2+}/[Ni(L^1)]^+$, compared with −1.42 V *vs.* S.C.E. for the couple $[Ni(L^2)]^{2+}/[Ni(L^2)]^+$. This result seems surprising, although spectral data suggest that the crystal-field splitting due to L^1 is smaller than that due to L^2,[4b] as substitution of the hydrogen atoms bound to the four ligating nitrogen atoms by methyl groups, which are electron donors, is expected to stabilize the higher oxidation state. We suggest that $[Ni(L^1)]^{2+}$ is considerably less stabilized by hydration, owing to its hydrophobic substituents, than $[Ni(L^2)]^{2+}$. A similar effect for analogous complexes in MeCN solution was recently reported.[1c]

In order to study fast redox reactions involving $[Ni(L^1)]^+$ we used the pulse-radiolysis technique[3c] using the linear accelerator at the Hebrew University of Jerusalem; for details, see ref. 7. $[Ni(L^1)]^{2+}$ was reduced by e^-_{aq} and $CO_2^{-\cdot}$,¶ and the rates of these reactions are summarized in Table 1. The electronic spectrum of $[Ni(L^1)]^+$ thus formed is identical to that of the product obtained electrochemically. The rates of reaction of $[Ni(L^1)]^+$ with O_2, $[Co(NH_3)_6]^{3+}$, and $[Ru(NH_3)_6]^{3+}$ were measured, and these outer-sphere reductions with $[Ni(L^1)]^+$ are about ten times slower than those[2] with $[Ni(L^2)]^+$, in agreement with their relative formal potentials. However, $[Ni(L^1)]^+$ does not seem to react with N_2O, possibly owing to

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‡ The decomposition of $[Ni(L^1)]^+$ under these conditions might be due to oxygen penetration into the flow-through optical cells used.

§ However, our electrochemical results (Figure 1) seem to indicate that $[Ni(L^2)]^+$ has a somewhat longer half-life than that reported by Tait *et al.*[2]

¶ Argon-saturated solutions containing 2—20 × 10^{-5} M-$[Ni(L^2)][ClO_4]_2$ and 0.1 M -Bu^tOH at pH 7.0 were used for the e^-_{aq} reductions, and argon- or N_2O-saturated solutions containing 2—10 × 10^{-4} M-$[Ni(L^1)][ClO_4]_2$ and 0.1 M-HCO_2Na at pH 4.7 and 11.5 for the $CO_2^{-\cdot}$ reductions.

** The shape of the voltammogram changes when the solution is in contact with mercury prior to the measurements. The cathodic peak is shifted to lower potentials, *i.e.*, to the hump detected on the cathodic peak in Figure 1. The voltammogram then indicates a nearly reversible electrode process. A detailed study[8] suggests that this change in the shape of the voltammogram is due to a surface-catalysed isomerization of $[Ni(L^1)]^{2+}$.

Table 1. Rate constants for the reactions of the nickel complexes of the ligands L^1 and L^2.

Reaction	L^{1a}	L^{2b}
$e^-_{aq} + NiL^{2+}$	$(8 \pm 1) \times 10^{10}$	5.6×10^{10}
$CO_2^{-\cdot} + NiL^{2+}$	$(4 \pm 2) \times 10^{6}$	5.7×10^{9}
$NiL^+ + Co(NH_3)_6^{3+}$	$(1.7 \pm 0.2) \times 10^{4}$	1.9×10^{5}
$NiL^+ + Ru(NH_3)_6^{3+}$	$(3.0 \pm 0.3) \times 10^{7}$	3.8×10^{8}
$NiL^+ + O_2$	$(4.0 \pm 1.5) \times 10^{7}$	1.6×10^{9}
$NiL^+ + N_2O$	< 0.1	3.9×10^{7}

[a] This work, units of $dm^3\ mol^{-1}\ s^{-1}$. [b] From ref. 2.

steric hindrance as the suggested reaction mechanism involves atom transfer.[2] Alternatively this might be due to a more positive value of the formal potential for the $[Ni(L^1)]^+/[Ni(L^1)]^{3+}$ couple. The low rate of reduction of $[Ni(L^1)]^{2+}$ by $CO_2^{-\cdot}$ is surprising in view of the relative formal potentials of $[Ni(L^1)]^{2+}$ and $[Ni(L^2)]^{2+}$ and seems to indicate that the reduction[2] of $[Ni(L^2)]^{2+}$ by $CO_2^{-\cdot}$ proceeds mainly *via* a bridged mechanism, but that of $[Ni(L^1)]^{2+}$ is hindered by steric factors.

In conclusion these preliminary results indicate that $[Ni(L^1)]^+$ is relatively stable over a wide pH range presumably owing to the inhibition of reaction (3) by the methyl substituents.

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