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Synthesis of [6-(1,4,7,10-Tetraaza-12-cyclotridecyl)-1,4,8,11-tetraazacyclotetradecane]dinickel(II) Perchlorate and Its Electrocatalytic Property for Water Reduction

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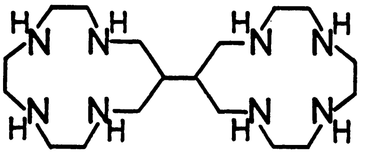
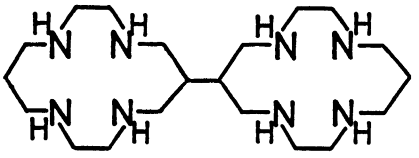
A new bimacrocyclic ligand, in which 13- and 14-membered rings are linked together by a C–C bond, 6-(1,4,7,10-tetraaza-12-cyclotridecyl)-1,4,8,11-tetraazacyclotetradecane (L^{13-14}), and its dinickel(II) complex, $[Ni^{II}_2L^{13-14}]^{4+}$, were synthesized. The absorption spectra and cyclic voltammograms of $[Ni^{II}_2L^{13-14}]^{4+}$ showed that it has properties of both the 13- and 14-membered rings. Cyclic voltammetry and controlled-potential electrolysis showed that $[Ni^{II}_2L^{13-14}]^{4+}$ can serve as an electrocatalyst for water reduction to produce H_2. The electrocatalytic efficiency for H_2 produclion at -1.5 V was found to be as follows: $[Ni^{II}_2L^{14-14}]^{4+}$ (L^{14-14}: 6,6′-bi(1,4,8,11-tetraazacyclotetradecane)) $>$ $[Ni^{II}_2L^{13-14}]^{4+} \approx [Ni^{II}L^{14}]^{2+}$ (L^{14}: 1,4,8,11-tetraazacyclotetradecane) $\gg$ $[Ni^{II}_2L^{13-13}]^{4+}$ (L^{13-13}: 12,12′-bi(1,4,7,10-tetraazacyclotridecane)).

The production of hydrogen from water is extremely important, especially for the chemical storage of light or electrical energy. For this purpose, a highly efficient catalytic system generating H_2 (and O_2) from water should be developed. Although the problem of overvoltage must be solved, some Ni(II) complexes with monomacrocyclic ligands are known to have a capability like that of an electrocatalyst.[1] Recently, Sauvage et al. investigated the electrocatalytic properties of a binuclear Ni(II) complex with biscyclam, $[Ni^{II}_2L^{14-14}]^{4+}$, in which two cyclams, L^{14}, are linked together by a C–C bond; they found that the bimacrocyclic complex, $[Ni^{II}_2L^{14-14}]^{4+}$, is a better catalyst than is the corresponding monomacrocyclic, $[Ni^{II}L^{14}]^{2+}$.[2] These findings prompted us to systematically study the electrocatalytic capabilities of this type of bimacrocyclic complexes.

We attempted to clarify how the electrocatalytic property of $[Ni^{II}_2L^{14-14}]^{4+}$ changes upon replacing the 14-membered macrocycles of $[Ni^{II}_2L^{14-14}]^{4+}$ with 13-membered ones. Thus, the dinickel(II) complexes with a bimacrocyclic ligand having two 13-membered rings, L^{13-13}, and with one having 13- and 14-membered rings, L^{13-14}, were required. However, the synthesis of the latter "nonsymmetric" ligand, L^{13-14}, has been unprecedented, to the best of our knowledge.

In this paper we describe the preparation of "nonsymmetric" ligand, L^{13-14}, and its dinickel(II) complex, as well as the electrocatalytic efficiencies of dinickel(II) complexes with L^{13-13}, L^{13-14}, and L^{14-14} for H_2 generation from water.


L^{13-13}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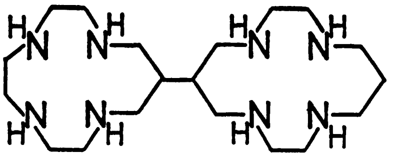
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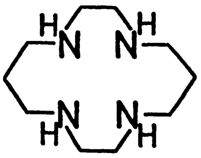
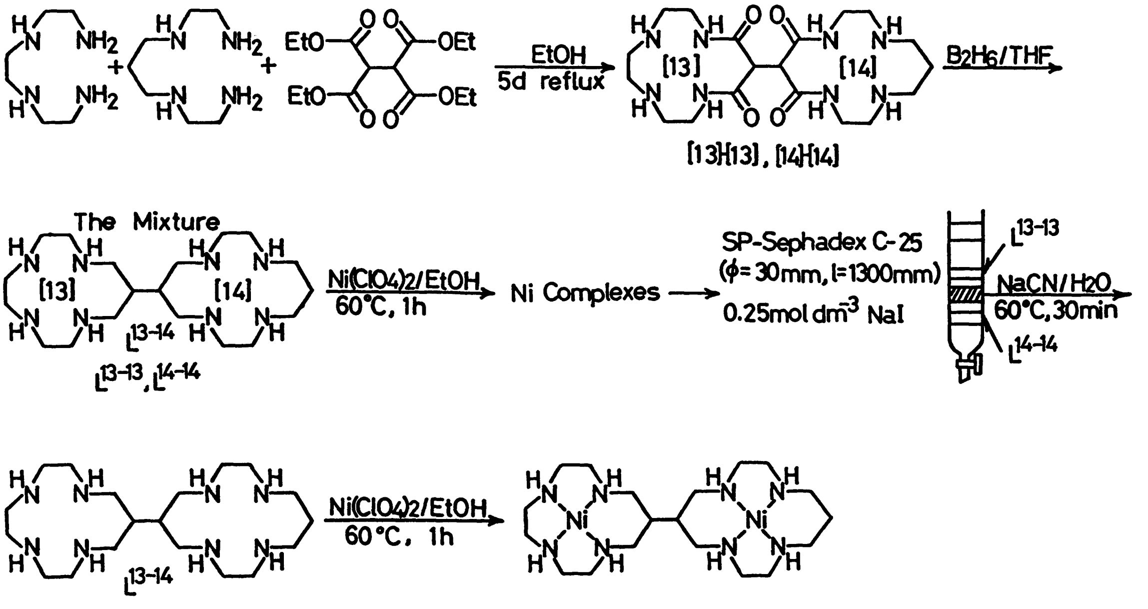

L^{14}

Results and Discussion

Synthesis of L^{13-14} and Its Dinickel(II) Complex. The synthetic route of the intending bimacrocyclic Ni(II) complex is shown in Scheme 1.

Statistic predominance was applied to the preparation of the bimacrocyclic ligand, L^{13-14}. Since the separation of L^{13-14} from the reaction mixture failed, its isolation was performed after conversion of the ligands into dinickel(II) complexes. This idea came from the following speculation based on experimental results.

It is known that in water both $[Ni^{II}L^{14}]^{2+}$ and $[Ni^{II}L^{13}]^{2+}$ (L^{13}: 1,5,8,11-tetraazacyclotridecane) are in equilibrium between square planar and octahedral forms; in the latter two water molecules coordinate to the Ni(II) ion; that the ratio of octahedral forms is slightly higher in $[Ni^{II}L^{14}]^{2+}$ (29%, 25 °C) than in $[Ni^{II}L^{13}]^{2+}$ (13%, 25 °C).[10] This means that the coordination of water to the 14-membered macrocyclic Ni(II) complex predominates slightly over that of the 13-membered one. If a similar relationship holds between the bimacrocyclic Ni(II) complexes and anionic ligands instead of water, $[Ni^{II}_2L^{14-14}]^{4+}$ favors octahedral form than does $[Ni^{II}_2L^{13-13}]^{4+}$. The cationic character of the



Scheme 1.

complex is thus least in $[\mathrm{Ni^{II}_2L^{14-14}}]^{4+}$, and most in $[\mathrm{Ni^{II}_2L^{13-13}}]^{4+}$. As a result, separation of the mixture by cation exchange chromatography may be possible.

Condensation between tetraethyl 1,1,2,2-ethanetetracarboxylate and a 1 : 1 mixture of 3,6-diazaoctane-1,8-diamine and 3,7-diazanonane-1,9-diamine, followed by reduction with $\mathrm{B_2H_6}$, afforded a mixture of three ligands: $\mathrm{L^{13-13}}$, $\mathrm{L^{13-14}}$, and $\mathrm{L^{14-14}}$ (see Experimental). The gas chromatogram of the mixture showed three peaks: the first was assigned to $\mathrm{L^{13-13}}$ (28%) and the third to $\mathrm{L^{14-14}}$ (16%) respectively, compared with the respective authentic samples (Fig. 1). We assigned the second peak to $\mathrm{L^{13-14}}$ (50%). Indeed, a FAB mass spectrum of the mixture showed three peaks at *m/z* 371, 385, and 399, which corresponded to$[\mathrm{M+H}]^+$ for $\mathrm{L^{13-13}}$, $\mathrm{L^{13-14}}$, and $\mathrm{L^{14-14}}$, respectively.

Separation of these three ligands was accomplished, when the ligands were converted into the dinickel(II) complexes and then chromatographed with SP-Sephadex C-25 cation-exchange resin using 0.25 mol dm^{-3} NaI as the eluent. As expected, $[\mathrm{Ni^{II}_2L^{14-14}}]^{4+}$ was eluted first, $[\mathrm{Ni^{II}_2L^{13-14}}]^{4+}$ second, and $[\mathrm{Ni^{II}_2L^{13-13}}]^{4+}$ last. This clear separation of the three bands indicates that the second band is not a mixture of $[\mathrm{Ni^{II}_2L^{14-14}}]^{4+}$ and $[\mathrm{Ni^{II}_2L^{13-13}}]^{4+}$, but $[\mathrm{Ni^{II}_2L^{13-14}}]^{4+}$, itself; this view is supported by the FAB mass spectrum of the free ligand obtained by treatment of the Ni(II) complex with NaCN (*m/z* 385, $[\mathrm{M+H}]^+$ for $\mathrm{L^{13-14}}$). Since a complete exchange of iodide into the perchlorate ion was tedious, an analytical sample of $[\mathrm{Ni^{II}_2L^{13-14}}](\mathrm{ClO_4})_4\cdot\mathrm{H_2O}$ was prepared by treatment of $\mathrm{L^{13-14}}$ with $\mathrm{Ni(ClO_4)_2\cdot 6H_2O}$.

The ligand, $\mathrm{L^{13-14}}$, and the $[\mathrm{Ni^{II}_2L^{13-14}}]^{4+}$ complex, thus isolated, were characterized as follows.

Although the ^{13}C NMR spectrum of $\mathrm{L^{13-14}}$ in $\mathrm{CDCl_3}$ was very similar to the sum of the spectrum of $\mathrm{L^{14-14}}$ and that of $\mathrm{L^{13-13}}$, small differences in the chemical shifts around the C–C bridge were observed between, $\mathrm{L^{13-14}}$, $\mathrm{L^{13-13}}$, and $\mathrm{L^{14-14}}$. The 100.614 MHz ^{13}C NMR spectrum of $\mathrm{L^{13-14}}$ in $\mathrm{D_2O}$ expectedly showed 11 signals (9 triplets and 2 doublets).

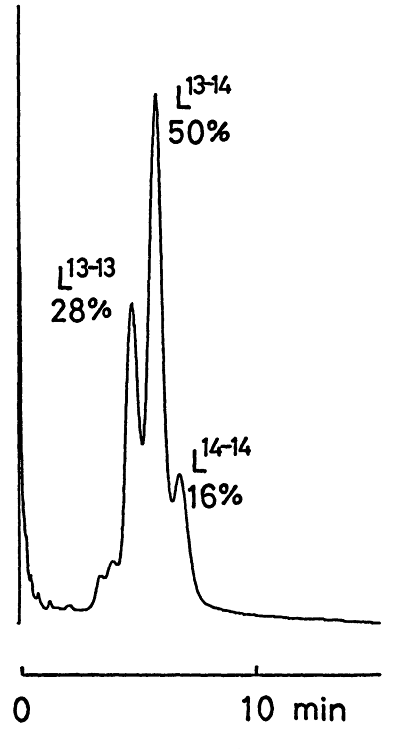


Fig. 1. Gas chromatogram of the mixture of ligands produced by reduction of the condensation product with tetramines (column: 1% OV-1, 0.25 m×2.6 mm; carrier gas: He; column temperature: 220 °C).

Figure 2 shows the absorption spectrum of $[\mathrm{Ni^{II}_2L^{13-14}}]^{4+}$ in an aqueous solution; it is almost equal to the

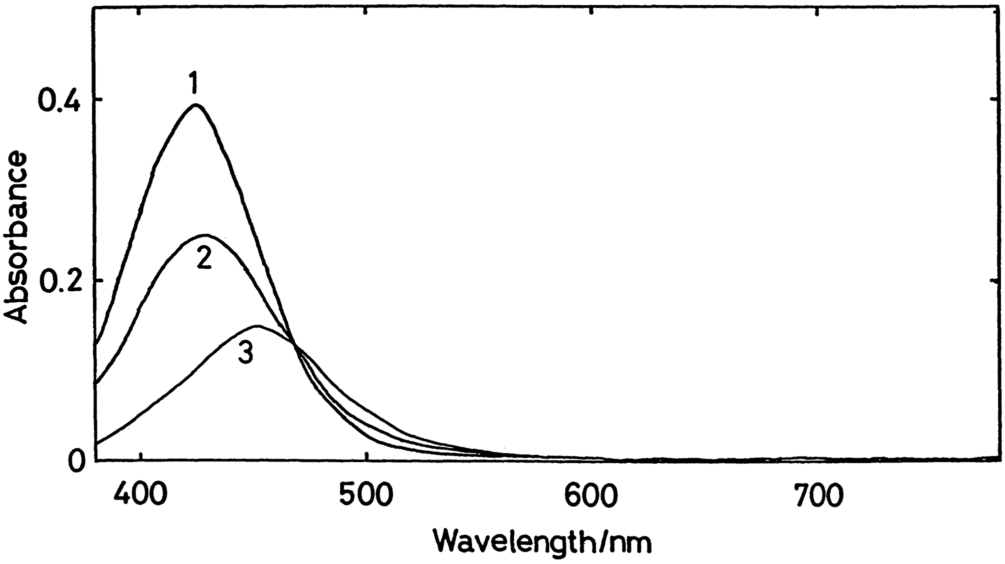


Fig. 2. Absorption spectra of 2×10^{-3} mol dm^{-3} $[Ni_2L^n]^{4+}$ (n=13—13 (1), 13—14 (2), 14—14 (3)) in water at 25 °C.

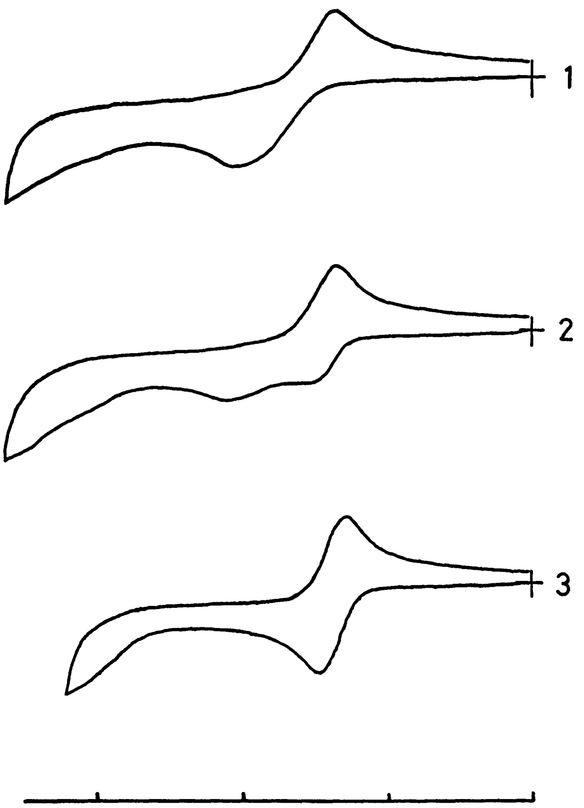


Fig. 3. Cyclic voltammograms of 2×10^{-3} mol dm^{-3} $[Ni_2L^n]^{4+}$ (n=13—13 (1), 13—14 (2), 14—14 (3)) in acetonitrile at 25 °C. Glassy carbon electrode. V vs. Ag–Ag$^+$ (0.01 mol dm^{-3} $AgNO_3$).

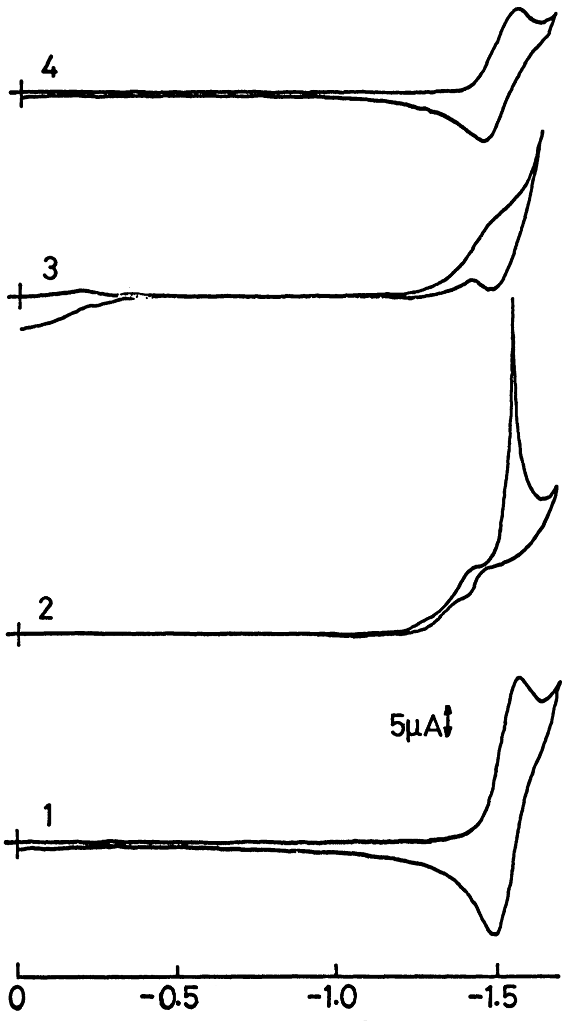


Fig. 4. Cyclic voltammograms of 5×10^{-3} mol dm^{-3} $[NiL^{14}]^{2+}$ (1) and 2×10^{-3} mol dm^{-3} $[Ni_2L^n]^{4+}$ (n= 13—13 (2), 13—14 (3), 14—14 (4)) in 0.1 mol dm^{-3} KCl aqueous solutions at 25 °C. HMDE.

average of the spectrum of $[Ni^{II}_2L^{14-14}]^{4+}$ and that of $[Ni^{II}_2L^{13-13}]^{4+}$. The same conclusion was also obtained by cyclic voltammetry. Figure 3 shows the cyclic voltammograms (CV) observed in the oxidation of $[Ni^{II}_2L^{13-14}]^{4+}$, $[Ni^{II}_2L^{14-14}]^{4+}$, and $[Ni^{II}_2L^{13-13}]^{4+}$, respectively, in acetonitrile. The CV of $[Ni^{II}_2L^{13-14}]^{4+}$ (E_{pa} 0.80_0; 1.04_5; E_{pc} 0.67_5 V) is again almost equal to the average of the spectrum of $[Ni^{II}_2L^{14-14}]^{4+}$ (E_{pa} 0.74_5; E_{pc} 0.64_5 V) and that of $[Ni^{II}_2L^{13-13}]^{4+}$ (E_{pa} 1.02_5; E_{pc} 0.68_0 V). $[Ni^{II}_2L^{13-14}]^{4+}$ was found to have properties of both the 13- and 14-membered rings.

Thus, a new bimacrocyclic ligand having 13- and 14-membered rings linked bythe C–C bond and its dinickel(II) complex were unequivocally obtained.

Electrocatalytic Properties. Figure 4 shows the CV's for the reduction of Ni(II) complexes in an aqueous solutions containing 0.1 mol dm^{-3} KCl as a supporting electrolyte. Our observations for $[Ni^{II}_2L^{14-14}]^{4+}$ were different from the results previously reported by Sauvage et al.;[2] they did not describe a quasi-reversible wave, but an irreversible wave for Ni^{II}/Ni^{I} couples in a neutral aqueous solution. We observed, here, a quasi-reversible wave at -1.50 V, accompanied by a small adsorption wave at -1.3 V, in a neutral aqueous solution of $[Ni^{II}_2L^{14-14}]^{4+}$ (E_{pc}=-1.55_1 V, E_{pa}=-1.44_9 V, HMDE, scan rate: 100 mV s^{-1}, 0.1 mol dm^{-3} KCl, 25 °C). A couple of cathodic and anodic peaks were observed; they were assignable to the couples of $[Ni^{II}Ni^{II}]/[Ni^{II}Ni^{I}]$ and $[Ni^{II}Ni^{I}]/[Ni^{I}Ni^{I}]$[11] by comparison with the Ni^{II}/Ni^{I} couple of $[Ni^{II}L^{14}]^{2+}$ (E_{pc}=-1.56 V, E_{pa}=-1.48 V), since two Ni(II) in the complex should be reduced at the very close potentials.[12] A similar quasi-reversible wave was observed when 0.1 mol dm^{-3} $NaClO_4$ was used as the supporting electrolyte. On the other hand, the 13-membered ring complex, $[Ni^{II}_2L^{13-13}]^{4+}$, does not show reversible waves, but a cathodic peak at -1.43 and a sharp irreversible peak at -1.54 V; the latter may be caused by strong adsorption of the complex to the Hg electrode. The mixed-ring complex, $[Ni^{II}_2L^{13-14}]^{4+}$, shows a broad wave comprising a broad cathodic peak around -1.47 V assignable to the reduction of two Ni(II) ions in the 13- and 14-membered rings, and an anodic peak around -1.47 V to the oxidation of Ni(I) formed in the 14-membered ring.

Figure 5 shows CV's measured under various conditions. When the solution contained only a supporting electrolyte (0.1 mol dm^{-3} KCl), a supporting electrolyte+phosphate buffer (pH 6.8), or a supporting electrolyte+$[Ni^{II}_2L^{14-14}]^{4+}$ (2×10^{-5} mol dm^{-3}), neither cathodic nor anodic peaks were observed in 0—-1.7 V. Only when both phosphate buffer and $[Ni^{II}_2L^{14-14}]^{4+}$ (2×10^{-5} mol dm^{-3}) was added to 0.1 mol dm^{-3} KCl solution, did a new wave appear at ca. -1.66 V. This was assigned

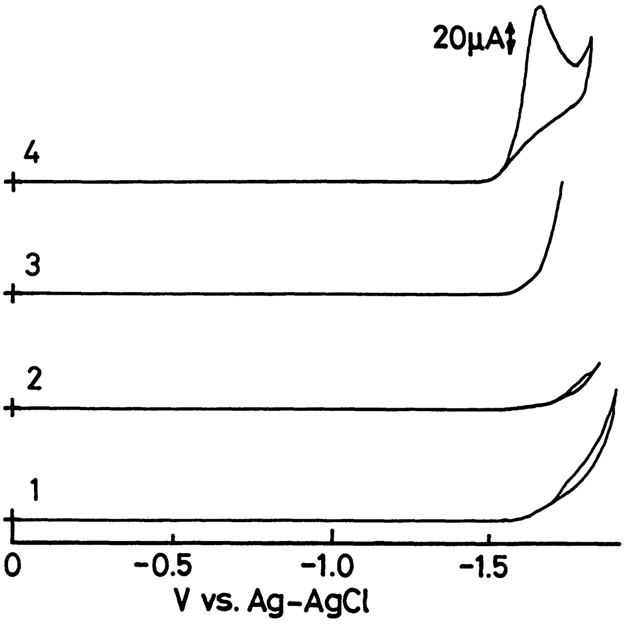


Fig. 5. Cyclic voltammograms of 0.1 mol dm^{-3} KCl aqueous solutions containing no buffers + no catalysts (1), phosphate buffer ($[HPO_4^{2-}]_T$=4×10^{-2} mol dm^{-3}, pH=6.8) (2), 2×10^{-5} mol dm^{-3} $[Ni_2L^{14-14}]^{4+}$ (3), and phosphate buffer ($[HPO_4^{2-}]_T$=4×10^{-2} mol dm^{-3}, pH=6.8)+2×10^{-5} mol dm^{-3} $[Ni_2L^{14-14}]^{4+}$ (4). T= 25 °C. HMDE.

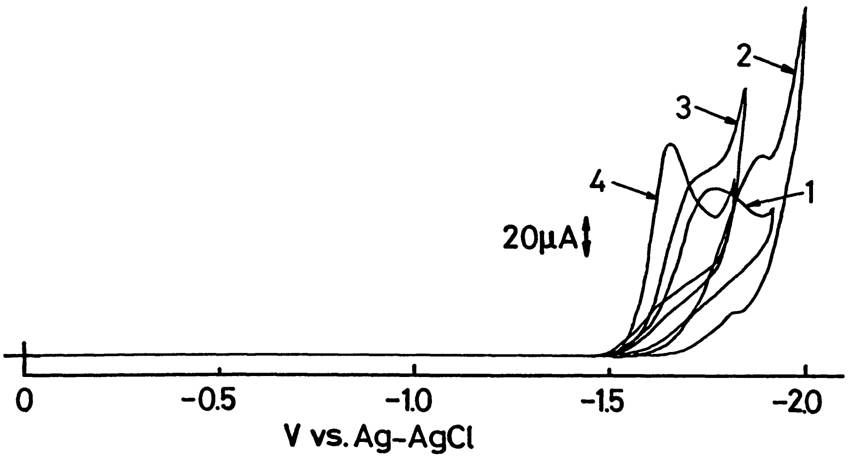


Fig. 6. Cyclic voltammograms of 0,1 mol dm^{-3} KCl aqueous solutions containing phosphate buffer ($[HPO_4^{2-}]_T$=4×10^{-2} mol dm^{-3}, pH=6.8) and 2×10^{-5} mol dm^{-3} Ni(II) complexes: $[NiL^{14}]^{2+}$ (1); $[Ni_2L^n]^{4+}$ (n= 13—13 (2), 13—14 (3), 14—14 (4)). T=25 °C. HMDE.

to the catalytic wave for water reduction, as reported previously.[2] Indeed, the controlled-potential electrolysis at the peak potential produced reasonable amounts of H_2, which was identical with a standard H_2 sample by gas chromatography. Similar catalytic waves were also observed upon the addition of $[Ni^{II}L^{14}]^{2+}$, $[Ni^{II}_2L^{13-14}]^{4+}$, or $[Ni^{II}_2L^{13-13}]^{4+}$.

Figure 6 shows the catalytic waves observed for solutions containing each Ni(II) complex (2×10^{-5} mol dm^{-3}), phosphate buffer, and 0.1 mol dm^{-3} KCl. The peak potentials, $(E_p)_{cata}$, of the catalytic waves are different among these Ni(II) complexes and their peak currents, $(i_p)_{cata}$, lie in 87—110 µA (see Table 1). According to the following order; $[Ni^{II}_2L^{13-13}]^{4+} < [Ni^{II}_2L^{13-14}]^{4+} \approx [Ni^{II}L^{14}]^{2+} < [Ni^{II}_2L^{14-14}]^{4+}$, $(E_p)_{cata}$ shifts toward the positive. As $(E_p)_{cata}$ becomes more positive, the wave begins to rise at a more positive potential; the overvoltage for the water reduction therefore becomes smaller. These results suggest that $[Ni^{II}_2L^{14-14}]^{4+}$ is the most favorable catalyst for H_2 production and that the electrocatalytic capability of $[Ni^{II}_2L^{13-14}]^{4+}$ should lie between those of $[Ni^{II}_2L^{14-14}]^{4+}$ and $[Ni^{II}_2L^{13-13}]^{4+}$, being close to that of mononuclear $[Ni^{II}L^{14}]^{2+}$.

The practical capabilities of the electrocatalysts could be evaluated by measurements of the amount of H_2 evolved by controlled-potential electrolysis: the greater was the amount of H_2, the more effective was the Ni(II) complex. The gas in the flask was analyzed by gas chromatography at an appropriate interval. In all cases, the amount of H_2 that evolved increased linearly with the electrolysis time.

We used a 1×10^{-4} mol dm^{-3} Ni(II) complex, where the concentration of the electrocatalyst has only a minor effect on the efficiency of H_2 production.[2] In the electrolysis at -1.5 V, only a small amount of H_2 is detected on a blank experiment in the absence of the Ni(II) complexes (Fig. 7). The addition of $[Ni^{II}_2L^{13-13}]^{4+}$ to a blank solution does not improve H_2 production, indicating that a Ni(II) complex with only 13-membered rings has a negligible electrocatalytic capability at -1.5 V. On the other hand, when the other Ni(II) complex with a 14-membered ring, $[Ni^{II}L^{14}]^{2+}$, $[Ni^{II}_2L^{13-14}]^{4+}$, or $[Ni^{II}_2L^{14-14}]^{4+}$, is added, a significantly larger amount of H_2 evolves compared with the case of a blank. The efficiency of binuclear $[Ni^{II}_2L^{14-14}]^{4+}$ is higher than that of mononuclear $[Ni^{II}L^{14}]^{2+}$ by about two times; this result, though the efficiency is somewhat lower in our experiments, is similar to that reported by Sauvage et al.[2] The capability of $[Ni^{II}_2L^{13-14}]^{4+}$ is almost equal to that of mononuclear $[Ni^{II}L^{14}]^{2+}$ and lies between those of $[Ni^{II}_2L^{14-14}]^{4+}$ and $[Ni^{II}_2L^{13-13}]^{4+}$. Thus, the order of the electrocatalytic capability derived from the controlled-potential electrolysis well corresponds to that predicted from $(E_p)_{cata}$ in CV experiments.

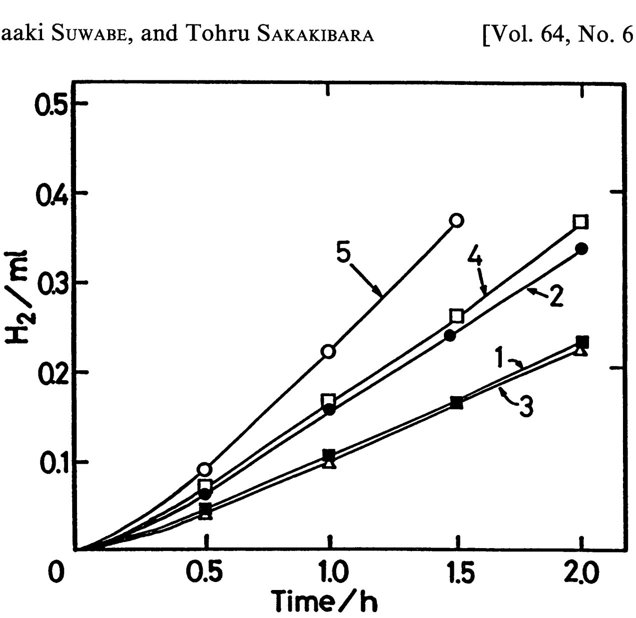


Fig. 7. Amount of H_2 evolved by the electrolysis at -1.5 V vs. Ag–AgCl. Electrolytic solutions contain only phosphate buffer ($[HPO_4^{2-}]_T$=0.2 mol dm^{-3}, pH=6.8) (1) and phosphate buffer+1×10^{-4} mol dm^{-3} Ni(II) complexes: $[NiL^{14}]^{2+}$ (2); $[Ni_2L^n]^{4+}$ (n=13—13 (3), 13—14 (4), 14—14 (5)). Mercury-pool electrode (8 cm^2). T=ca. 23 °C.

Table 1. Electrochemical Data of Catalytic Waves[a)]

Complex	$(E_p)_{cata}$/V	$(i_p)_{cata}$/µA
$[Ni^{II}L^{14}]^{2+}$	−1.77	87
$[Ni^{II}_2L^{14-14}]^{4+}$	−1.66	110
$[Ni^{II}_2L^{13-14}]^{4+}$	−1.75	95
$[Ni^{II}_2L^{13-13}]^{4+}$	−1.89	104

a) Solutions contained 0.1 mol dm^{-3} KCl, phosphate buffer ($[HPO_4^{2-}]_T$=4×10^{-2} mol dm^{-3}, pH 6.8), and 2×10^{-5} mol dm^{-3} Ni(II) complex.

These data obtained herein undoubtedly show that the electrocatalytic capability strongly depends on the ring sizes of bimacrocyclic Ni(II) complexes, where the capability falls as 14-membered rings are replaced by 13-membered rings, i.e., the "symmetric" bimacrocycle, $[Ni^{II}_2L^{14-14}]^{4+}$, is the most favorable for H_2 generation.

Experimental

Materials. The procedures for preparations of the ligand L^{13-14} and of its dinickel(II) complex are as follows.

Tetraoxo Derivatives: Tetraethyl 1,1,2,2-ethanetetracarboxylate (25.5 g, 0.08 mol) was dissolved in dry ethanol (1.6 dm^3) under an N_2 atmosphere, to which was added dropwise in 30 min a mixture of 3,6-diazaoctane-1,8-diamine (11.7 g, 0.08 mol) and 3,7-diazanonane-1,9-diamine (12.8 g, 0.08 mol). The solution was heated under reflux for 5 d. White precipitates which formed were filtered, washed with cold ethanol, and dried over P_2O_5 in a vacuum to give a mixture consisting of three tetraoxo derivatives, 6-(11,13-dioxo-1,4,7,10-tetraaza-12-cyclotridecyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione), 12,12′-bi[1,4,7,10-tetraazacyclotridecane-11,13-dione], and 6,6′-bi[1,4,8,11-tetraazacyclotetradecane-5,7-dione] in 18% yield. Since several attempts to separate the mixture failed, a crude mixture was subjected to the following procedures.

Reduction of the Mixture of Tetraoxo Derivatives: The mixture (4.0 g) of tetraoxo derivatives was suspended in tetrahydrofuran (300 cm^3) under an N_2 atmosphere, to which was added B_2H_6 (240 cm^3, 1 mol dm^{-3} in tetrahydrofuran). After the solution was heated under reflux for 6 h, B_2H_6 (160 cm^3) was again added; refluxing was continued for additional 12 h. After the solution was cooled to room temperature, methanol (200 cm^3) was carefully added dropwise (*CAUTION*: this reaction can be explosive) to quench any excess B_2H_6. The resulting solution was evaporated to dryness. To the residue, conc. HCl (30 cm^3), water (60 cm^3), and methanol (160 cm^3) were added; the solution was then evaporated to dryness, this treatment being repeated five times in order to remove boric acid as trimethyl borate. To the residue, thus obtained, was added NaOH (50 cm^3, 1 mol dm^{-3}, pH>13). The reduction products were extracted five times with $CHCl_3$ (100 cm^3). The combined extracts were dried over anhydrous Na_2SO_4 over night and evaporated to dryness to give a white residue, a mixture of three bimacrocyclic ligands: L^{13-13}, L^{13-14}, and L^{14-14}. Yield: 92%.

Separation of the Mixture of Ligands: A mixture (1.5 g) of L^{13-13}, L^{13-14}, and L^{14-14} was dissolved in ethanol (80 cm^3), to which was added nickel(II) perchlorate hexahydrates (2.85 g, 7.8 mmol) in ethanol (160 cm^3). The mixture was stirred at 60 °C for 1 h to give yellow precipitates. The precipitates were suspended in a small amount of water and passed through a column of Cl-form anion-exchange resin (Amberlite IRA-410, ϕ=30 mm, l=300 mm) to exchange the counter ions from perchlorates to chlorides. The resulting clear solution was chromatographed with a cation-exchange column (SP-Sephadex C-25, ϕ=30 mm, l=1300 mm), with a 0.25 mol dm^{-3} sodium iodide solution as the eluent, to give three orange bands. The first and third bands were assigned to $[\mathrm{Ni^{II}}_2L^{14-14}]^{4+}$ and $[\mathrm{Ni^{II}}_2L^{13-13}]^{4+}$ respectively by comparison with respective authentic samples (see below). The second eluate was concentrated to ca. 200 cm^3, adjusted to pH>13 by adding NaOH, and heated at 60 °C. To the solution was added NaCN (2.4 g, 0.049 mol); the solution was stirred at 60 °C for 30 min. After being cooled to room temperature, the solution was extracted with $CHCl_3$ (100 cm^3) four times. The combined extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness to give a pale-yellow residue of the free ligand, L^{13-14}, in 13 % yield. An analytical sample of hydrochloride was prepared by the following treatment. The residue was dissolved in a small amount of ethanol, to which was added conc. HCl (1 cm^3) to give a white precipitate. The precipitate was washed with dry ethanol and dried over P_2O_5 in a vacuum.

$L^{13-14}\cdot 8HCl\cdot 1.5H_2O$: Found: C, 32.58; H, 8.01; N, 15.77%. Calcd for $C_{19}H_{44}N_8\cdot 8HCl\cdot 1.5H_2O$: C, 32.45; H, 7.88; N, 15.93%.

L^{13-14}: ^{13}C NMR ($CDCl_3$, TMS) δ=29.4 (t), 42.1 (d), 42.3 (d), 47.6 (2t), 49.1 (t), 49.6 (2t), 51.0 (t), 54.5 (t), and 54.9 (t). FAB MS m/z 385 $[M+H]^+$.

$[\mathrm{Ni^{II}}_2L^{13-14}](ClO_4)_4\cdot H_2O$: The free ligand L^{13-14} (0.1 g, 0.26 mmol) was dissolved in ethanol (5 cm^3), to which was added nickel(II) perchlorate hexahydrates (0.19 g, 0.52 mmol) in ethanol (10 cm^3). The mixture was stirred at 60 °C for 1 h, cooled at room temperature, and filtered to give yellow precipitates. The precipitates were recrystallized from a small amount of water to give plate crystals, which were washed with cold water and dried at 80 °C over P_2O_5 in a vacuum. Yield: 42%. Found: C, 24.89; H, 4.91; N, 12.34%. Calcd for $C_{19}H_{44}N_8Ni_2Cl_4O_{16}\cdot H_2O$: C, 24.86; H, 5.05; N, 12.21%. VIS (H_2O) 428 (ε 130), (CH_3NO_2) 431 nm (167 mol dm^3 cm^{-1}).

$[\mathrm{Ni^{II}}_2L^{14-14}](ClO_4)_4\cdot H_2O$: L^{14-14} was prepared according to a method described in the literature.[6] The dinickel(II) complex of L^{14-14} was prepared by the analogous method described above. Found: C, 25.66; H, 5.02; N, 11.85%. Calcd for $C_{20}H_{46}N_8Ni_2Cl_4O_{16}\cdot H_2O$: C, 25.78; H, 5.19; N, 12.03%. VIS (H_2O) 450 (ε 77), (CH_3NO_2) 456nm (113 mol^{-1} cm^3 cm^{-1}).

L^{14-14}: ^{13}C NMR ($CDCl_3$, TMS) δ=29.1 (t), 42.7 (d), 49.2 (t), 50.7 (t), and 54.8 (t).

$[\mathrm{Ni^{II}}_2L^{13-13}](ClO_4)_4\cdot H_2O$: L^{13-13} and its dinickel(II) complex were prepared by the analogous method as described in the preparation of $[\mathrm{Ni^{II}}_2L^{14-14}](ClO_4)_4\cdot H_2O$. Found: C, 24.13; H, 4.72; N, 12.48%. Calcd for $C_{18}H_{42}N_8Ni_2Cl_4O_{16}\cdot H_2O$: C, 23.92; H, 4.91; N, 12.40%. VIS (H_2O) 424 (ε 185), (CH_3NO_2) 427 nm (203 mol dm^3 cm^{-1}).

L^{13-13}: ^{13}C NMR ($CDCl_3$, TMS) δ=42.0 (d), 47.3 (t), 49.0 (t), and 54.1 (t).

Measurements. The visible absorption spectra were measured with a Hitachi 340 spectrophotometer. ^{13}C NMR spectra were recorded with JEOL FX90Q or Brucker AM400 spectrometers. FAB mass spectra were measured with a JEOL DX303 spectrometer.

Cyclic voltammograms for the oxidation of dinickel(II) complexes were measured according to a method described in our previous paper.[9] Cyclic voltammograms for the reduction were carried out by using a Yanagimoto Polarographic Analyzer P-1100. A hanging mercury electrode (Metrohm EA-290 equipped with glass capillary EA-1053) and Pt spiral electrode were used as working electrode and counter electrode respectively.

Controlled-potential electrolyses were performed at room temperature (ca. 23 °C), in a gas-tight electrolysis cell under one atmosphere of N_2 with a Fuso potentiostat 315A. The gas-tight cell was a 100 cm^3, three-necked, round-bottomed flask equipped with two side arms. The working electrode used in all the experiments was mercury (8 cm^2) which had been distilled twice. The counter electrode (Pt) and the reference electrode (Ag/AgCl) were separated from the working electrode compartment by a glass frit. The gases occupied 95 cm^3 of the cell volume. Before electrolysis, the aqueous solution (50 cm^3) was degassed by bubbling N_2 for 30 min, after which the admission tap was turned off, the internal pressure within the electrolysis cell being kept equal to 1 atm by means of an oil valve.

Gas samples (0.5 cm^3), taken at various intervals with a gas-tight syringe through a septum, were analyzed on a Shimadzu GC-14A gas chromatograph with a thermal conductivity detector by using a 2.1 m×3 mm column packed with molecular sieve 5A at 60 °C using argon as carrier gas.

References

1) B. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, **102**, 7361 (1980).

2) J. P. Collin, A. Jouaiti, and J. P. Sauvage, *Inorg. Chem.*, **27**, 1986 (1988).

3) A. M. Tait, M. Z. Hoffman, and E. Hayon, *Inorg. Chem.*, **15**, 934 (1976); D. Meyerstein, *Acc. Chem. Res.*, **11**, 43 (1978), and references therein; J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos, and M. Calvin, *J. Chem. Soc., Dalton Trans.*, **1987**, 2105.

4) I. Murase, K. Hamada, and S. Kida, *Inorg. Chim. Acta*, **54**, L171 (1981); I. Murase, K. Hamada, S. Ueno, and S. Kida, *Synth. React. Inorg. Met.-Org. Chem.*, **13**, 191 (1983); I.

Murase, S. Ueno, and S. Kida, *Inorg. Chim. Acta,* **111**, 57 (1986).

5) M. Ciampolini, M. Micheloni, N. Nardi, F. Vizza, A. Buttafava, L. Fabbrizzi, and A. Perotti, *J. Chem. Soc., Chem. Commun.,* **1984**, 998; L. Fabbrizzi, F. Forlini, A. Perotti, and B. Seghi, *Inorg. Chem.,* **23**, 807 (1984); A. Buttafava, L. Fabbrizzi, A. Perotti, A. Poggi, and B. Seghi, *Inorg. Chem.,* **23**, 3917 (1984); R. Schneider, A. Riesen, and T. A. Kaden, *Helv. Chim. Acta,* **68**, 53 (1985).

6) L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden, and L. Siegfried, *Inorg. Chem.,* **25**, 2671 (1986); L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden, and L. C. Siegfried, *J. Chem. Soc., Dalton Trans.,* **1987**, 2631.

7) E. K. Barefield, D. Chueng, D. G. Van Derveer, and F. J. Wagner, *J. Chem. Soc., Chem. Commun.,* **1981**, 302.

8) K. Mochizuki, K. Toriumi, and T. Ito, *Bull. Chem. Soc. Jpn.,* **57**, 881 (1984); K. Mochizuki, *Bull. Chem. Soc. Jpn.,* **61**, 1023 (1988); K. Mochizuki and Y. Endoh, *Bull. Chem. Soc. Jpn.,* **62**, 936 (1989).

9) K. Mochizuki and M. Fujimoto, *Bull. Chem. Soc. Jpn.,* **58**, 1520 (1985).

10) L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.,* **1979**, 1857.

11) Assuming the theoretical separation (36 mV) of the two couples, $E^1_{1/2}$ for $[\mathrm{Ni^{II}Ni^{II}}]/[\mathrm{Ni^{II}Ni^{I}}]$ and $E^2_{1/2}$ for $[\mathrm{Ni^{II}Ni^{I}}]/[\mathrm{Ni^{I}Ni^{I}}]$ can be calculated to be −1.48 and −1.52 V respectively. $E^1_{1/2}$ seems to shift to rather positive side compared with $E_{1/2}$ (−1.52 V) of $\mathrm{Ni^{II}/Ni^{I}}$ of $[\mathrm{Ni^{II}L^{14}}]^{2+}$. One Ni(II) in $[\mathrm{Ni^{II}}_2\mathrm{L}^{14-14}]^{4+}$ might be reduced easier than $[\mathrm{Ni^{II}L^{14}}]^{2+}$.

12) It is reported that two Ni(II) in $[\mathrm{Ni^{II}}_2\mathrm{L}^{14-14}]^{4+}$ are oxidized at very close potentials (see Ref. 6).