Synthesis and Characterization of a Di-*N*-hydroxyethylated Tetraaza Macrocycle and its Nickel(II) and Copper(II) Complexes: Crystal Structure of the Nickel(II) Complex†

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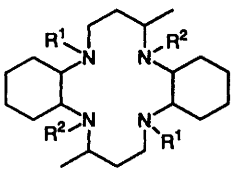
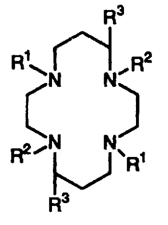
The one-step reaction of 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane (L^1) with 2-bromoethanol produced the macrocycle 2,13-bis(2-hydroxyethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane (L^2) in which two 2-hydroxyethyl groups are appended. The nickel(II) and copper(II) complexes of L^2 have been prepared and characterized. The crystal structure of $[NiL^2][ClO_4]_2$ shows that the complex is exactly centrosymmetric and the metal centre has a slightly distorted octahedral geometry with two oxygen atoms of the pendant arms at the axial positions. However, spectra and redox potentials of $[CuL^2][ClO_4]_2$ indicate that the complex has a planar geometry without co-ordination of the pendant arms. The macrocycle L^2 reacts more slowly with copper(II) ion than does L^1 and the resulting complex dissociates very slowly even at low pH. Crystal data for $[NiL^2][ClO_4]_2$: monoclinic, space group $P2_1/n$, $a = 9.128(2)$, $b = 18.141(3)$, $c = 9.256(2)$ Å, $\beta = 101.69(1)°$, $Z = 2$, $R = 0.057$ and $R' = 0.060$ for 1993 independent reflections with $I > 3\sigma(I)$.

A variety of research has concerned synthetic, kinetic, and structural aspects of polyaza macrocyclic compounds with functional pendant arms such as hydroxyl, amino and carboxylato groups.[1–16] It has been widely observed that the introduction of additional functional groups into polyaza macrocyclic compounds causes a considerable change in chemical properties and structures. For example, although most 14-membered tetraaza macrocycles such as 1,4,8,11-tetraazacyclotetradecane (L^3) react very slowly with nickel(II) or copper(II) ions and the resulting metal complexes are scarcely decomposed even at low pH, the fully *N*-hydroxyethylated macrocycle 1,4,8,11-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane (L^4) shows greatly increased lability in both formation and dissociation reactions of its complexes.[11–13] The increased lability of L^4, compared to L^3, has been attributed to the presence of the hydroxyethyl groups which promote such reactions.[11–13]

Partially *N*-functionalized tetraaza macrocycles and their complexes have been studied less extensively than fully *N*-functionalized analogues.[14–16] This may be due to the fact that partial *N*-substitution of tetraaza macrocycles such as L^3 is complicated and generally requires several steps:[14–17] as far as we know, partial *N*-hydroxyethylation of L^3 has not been reported to date. In this work, we attempted the synthesis of the di-*N*-hydroxyethylated macrocycle 2,13-bis(2-hydroxyethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane (L^2) by direct reaction of 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.^{1,4}0^{7,12}]docosane L^1,[18] which contains both cyclohexane rings and the C-methyl groups, with $BrCH_2CH_2OH$, to investigate how the properties of the ligand and its metal complexes are influenced by the pendant arms. Interestingly, it was found that the effects of the hydroxyethyl groups on the kinetic behaviour of L^2 and its complexes are different from those of the fully *N*-hydroxyethylated macrocycle L^4 and its complexes. This paper reports the synthesis and properties of L^2 and its nickel(II) and copper(II) complexes. The crystal structure of $[NiL^2][ClO_4]_2$ is also reported.



	R^1	R^2
L^1	H	H
L^2	CH_2CH_2OH	H



	R^1	R^2	R^3
L^3	H	H	H
L^4	CH_2CH_2OH	CH_2CH_2OH	H
L^5	Et	H	Me

Experimental

Measurements.—IR spectra were recorded as either Nujol mulls or KBr pellets on a Shimadzu IR-440 spectrophotometer, electronic spectra with a Shimadzu UV-160 spectrophotometer, conductance measurements with a Metrohm Herisau Conductometer E518, NMR spectra with a Bruker WP 300 FT NMR spectrometer and mass spectra with a Kratos 25-RFA GC-mass spectrometer. Elemental analyses were performed at the Kolon R. & D. Center, Kumi, Korea. Magnetic susceptibilities were measured with a Johnson Matthey MK-1 magnetic susceptibility balance. Molar susceptibilities were corrected for diamagnetism of the ligand and the anions by use of Pascal's constants. Cyclic voltammograms were recorded using a Yanaco p-1000 voltammetric analyzer equipped with a FG-121B function generator and a Watanabe X-Y recorder. The electrochemical measurements were conducted in oxygen-free 0.1 mol dm^{-3} NBu_4ClO_4 acetonitrile solutions at 20 °C.

Kinetic measurements of the formation of the copper(II) complexes of L^1 and L^2 were carried out in acetate buffer solutions (pH 5.4) of methanol–water (1 : 1) at 20 °C. The initial concentrations of the ligands and the metal ion in the reaction mixtures are 1.0×10^{-3} and 2.0×10^{-2} mol dm^{-3}, respectively.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

The reaction was monitored using the absorbance increase at 520 (L^1) or 530 nm (L^2). The acid dissociation rates of the complexes were measured using the absorbance decrease of the complexes in 0.3 mol dm^{-3} $HClO_4$ solutions.

Materials.—All chemicals used in syntheses were of reagent grade and were used without further purification. The macrocyclic ligand L^1 was prepared as described previously.[18]

Syntheses.—L^2. An acetonitrile suspension of L^1 (6.0 g, 0.018 mol), 2-bromoethanol (98%, 10.0 cm^3, 0.13 mol), and $NaHCO_3$ (13.1 g, 1.56 mol) was heated at reflux over 2 d. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was redissolved in a minimum volume of hot methanol and then an equal volume of 0.1 mol dm^{-3} NaOH aqueous solution was added to the solution. The white solid formed was filtered, washed with water, and dried in air (Yield: > 70%), m.p. 246 °C, *m/z* 425 (Found: C, 67.95; H, 11.60; N, 13.00. $C_{24}H_{48}N_4O_2$ requires C, 67.75; H, 11.30, N, 13.20%). IR: 3120 [ν(N–H)] and 3280 cm^{-1} [ν(O–H)]. NMR (CD_3NO_2): ^1H, δ 1.05 (d, Me); ^{13}C, δ 18.9 (Me), 22.0, 25.3, 25.6, 29.9, 33.4, 50.0, 50.2, 50.4, 54.1(d) and 60.1.

$[NiL^2][ClO_4]_2$. A methanol solution (30 cm^3) of $Ni(O_2CMe)_2{\cdot}4H_2O$ (2.0 g, 8 mmol) and L^2 (2.0 g, 5 mmol) was heated at reflux for 30 min and then cooled to room temperature. After the addition of excess $LiClO_4$ or $HClO_4$, the mixture was stored in a refrigerator until a pale purple precipitate formed. The product was filtered and recrystallized from hot water–acetonitrile (yield: ≈ 90%) (Found: C, 42.90; H, 7.35; N, 8.10. $C_{24}H_{48}Cl_2N_4NiO_{10}$ requires C, 42.25; H, 7.10; N, 8.20%). IR: 3235 [ν(N–H)] and 3360 cm^{-1} [ν(O–H)].

$[CuL^2][ClO_4]_2$. This compound was prepared by a method similar to that for the nickel(II) complex, except that $Cu(O_2CMe)_2{\cdot}H_2O$ (2.0 g) was employed instead of $Ni(O_2CMe)_2{\cdot}6H_2O$ (yield: ≈ 90%) (Found: C, 42.30; H, 7.30; N, 8.00. $C_{24}H_{48}Cl_2CuN_4O_{10}$ requires C, 41.95; H, 7.05; N, 8.15%). IR: 3250 [ν(N–H)] and 3360 cm^{-1} [ν(O–H)].

Crystallography.—Pale purple crystals of $[NiL^2][ClO_4]_2$ for X-ray study was grown from water–acetonitrile. A crystal (0.4 × 0.35 × 0.3 mm) was mounted on an Enraf-Nonius CAD4 diffractometer. X-Ray data were collected using graphite-monochromated Mo-Kα radiation at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The intensities of three standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. All the calculations were carried out with the Enraf-Nonius MOLEN Package.[19] The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections (DIFABS) were also applied. The structure was solved by a combination of Patterson and Fourier difference methods and refined by full-matrix least-squares methods. All the non-hydrogen atoms were refined anisotopically. The positions of hydrogen atoms were idealized [*d*(C–H) = 0.95 Å] and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter 1.2 times that of the attached atom. The final cycle of refinement led to the *R* indices listed in Table 1. The final positional parameters for $[NiL^2][ClO_4]_2$ are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Table 1 Crystal and refinement data for $[NiL^2][ClO_4]_2$

Formula	$C_{24}H_{48}Cl_2N_4NiO_{10}$
M	682.29
Crystal symmetry	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	9.128(2)
b/Å	18.141(3)
c/Å	9.256(2)
β/°	101.69(1)
U/Å^3	1501.2(5)
Z	2
F(000)	724
T/°C	23
D_c/g cm^{-3}	1.506
λ(Mo-Kα)/Å	0.710 73
μ/cm^{-1}	8.83
Crystal size/mm	0.4 × 0.35 × 0.3
Crystal colour	Pale purple
Scan mode	ω
ω-Scan width/°	0.75 + 0.35 tan θ
2θ range/°	3–50
No. of data collected	2915
No. of unique data	2735
No. of unique data with $I > 3\sigma(I)$	1993
No. of variables	187
R^a	0.057
R'^b	0.060
Goodness of fit	0.75

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 4F_o{}^2/\sigma^2(F_o{}^2)$; $\sigma(F_o{}^2) = [\sigma^2(I) + (pF_o{}^2)^2]^{\frac{1}{2}}$; $p = 0.04$.

Results and Discussion

Synthesis.—Direct reaction of L^1 with an excess of 2-bromoethanol in the presence of $NaHCO_3$, was expected to produce a mixture of various types of *N*-hydroxyethylated macrocycles. However, the only product isolated from the reaction mixture was the di-*N*-substituted macrocycle L^2 even after prolonged heating (> 10 days) at reflux of the reaction mixture. Furthermore, the yield was relatively high (> 70%). All efforts to isolate any other partially or fully *N*-hydroxyethylated macrocycles were unsuccessful. It is somewhat interesting to observe that the introduction of the hydroxyethyl group into the nitrogens adjacent to the methylated carbons does not take place under the present experimental conditions. This can be attributed to the steric hindrance caused by the methyl groups and the cyclohexane rings fused to the macrocycle.

The macrocycle L^2 is extremely stable in the solid state and readily dissolves in methanol, diethyl ether and chloroform. The mass spectrum of L^2 gives an *m/z* value of 425, which is in accord with the molecular weight of the macrocycle. The ^1H NMR spectrum of L^2 shows only one doublet centred at δ 1.05 for the two methyl groups and the ^{13}C NMR spectrum shows 12 peaks (see Experimental section). These data indicate that although the macrocycle contains various chiral centres, the isolated ligand is a single isomer with a symmetrical arrangement of the carbon atoms. The structure of L^2 was confirmed by a crystal structure of its nickel(III) complex (see below).

The nickel(II) and copper(II) complexes of L^2 are readily prepared by heating at reflux methanol solutions of the ligand and the corresponding metal ions.

Crystal Structure of $[NiL^2][ClO_4]_2$.—The ORTEP drawing (Fig. 1) of the complex cation $[NiL^2]^{2+}$ shows that the two hydroxyethyl groups are attached to the less sterically hindered nitrogen atoms of the ligand. Four nitrogen atoms of the macrocycle and two oxygen atoms of the hydroxyethyl groups are co-ordinated to the metal ion, and the complex has a *trans*-octahedral geometry with an inversion centre. The macrocyclic ligand adopts the *trans*-III stereochemistry. The six-membered chelate rings and the cyclohexane rings adopt stable chair conformations. The hydroxyethyl group and the methyl group in a six-membered chelate ring are *anti* with respect to the plane.

Table 2 Positional parameters for the non-hydrogen atoms of $[NiL^2][ClO_4]_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.000	0.500	0.500	C(3)	0.093 1(7)	0.274 5(4)	0.874 3(7)
Cl	0.371 8(2)	0.634 77(9)	0.234 3(2)	C(4)	0.193 0(7)	0.328 0(4)	0.973 8(7)
O(1)	0.220 9(4)	0.503 6(2)	0.453 0(4)	C(5)	0.145 2(7)	0.408 1(4)	0.933 2(6)
O(2)	0.396 8(7)	0.617 2(4)	0.388 3(6)	C(6)	0.144 1(6)	0.424 5(3)	0.771 1(6)
O(3)	0.271 7(8)	0.578 9(4)	0.169 4(7)	C(7)	0.170 6(7)	0.562 6(3)	0.803 4(6)
O(4)	0.503 8(6)	0.636 8(5)	0.186 5(7)	C(8)	0.088 5(7)	0.634 7(3)	0.753 1(6)
O(5)	0.293 0(9)	0.698 7(4)	0.206(1)	C(9)	−0.066 9(6)	0.344 6(3)	0.409 3(6)
N(1)	0.052 4(4)	0.387 3(2)	0.510 9(5)	C(10)	0.205 2(6)	0.373 7(3)	0.476 8(6)
N(2)	0.081 1(5)	0.499 0(3)	0.727 0(4)	C(11)	0.258 2(6)	0.434 9(3)	0.391 5(6)
C(1)	0.051 8(6)	0.367 9(3)	0.668 2(6)	C(12)	0.333 1(7)	0.562 4(4)	0.783 8(8)
C(2)	0.098 9(7)	0.288 6(3)	0.712 2(7)				

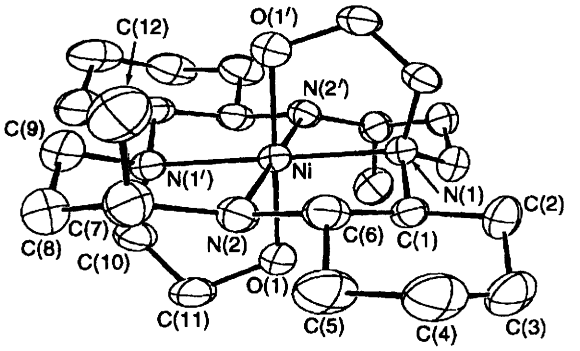

Fig. 1 An ORTEP drawing of $[NiL^2]^{2+}$ in $[NiL^2][ClO_4]_2$ with the atomic labelling scheme

Table 3 Selected bond distances (Å) and angles (°) for $[NiL^2][ClO_4]_2$ with e.s.d.s in parentheses *

Ni–O(1)	2.149(4)	Ni–N(1)	2.099(4)
Ni–N(2)	2.085(4)	O(1)–C(11)	1.439(7)
N(1)–Ni–N(2)	85.0(2)	N(1)–Ni–N(2′)	95.0(2)
N(1)–Ni–N(1′)	180.0(0)	O(1)–Ni–O(1′)	180.0(0)
N(1)–Ni–O(1)	79.9(2)	N(2)–Ni–O(1′)	87.2(1)
Ni–O(1)–C(11)	111.2(3)	Ni–N(1)–C(1)	103.3(3)
Ni–N(1)–C(9)	110.1(3)	Ni–N(1)–C(10)	111.1(3)

* Primed atoms are related to the corresponding unprimed atoms by inversion.

Table 4 Electronic spectral data [a]

Compound	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$[NiL^2][ClO_4]_2$	516(7.2), 323(18) 520(6.8),[b] 335(16)[b]
$[NiL^4]^{2+}$ [c]	595(13.5), 366(34)
$[CuL^2][ClO_4]_2$	527(110) 523(98)[b] 522(98)[d] 535[e]
$[CuL^4]^{2+}$ [c]	645
$[CuL^5]^{2+}$ [f]	525(159) 524(148)[b]

[a] In water at 20 °C unless otherwise specified. [b] In acetonitrile. [c] Ref. 12. [d] In nitromethane. [e] Nujol mull. [f] Ref. 23.

Selected bond distances and angles of the complex are listed in Table 3. The Ni–N(1) (tertiary) distance [2.099(4) Å] is somewhat longer than that of Ni–N(2) (secondary) [2.085(4) Å]. The Ni–N and Ni–O distances are typical for high-spin octahedral nickel(II) complexes with tetraaza macrocyclic ligands.[7,12,15,20,21] However, the average Ni–N (2.092 Å) and Ni–O (2.149 Å) distances are *ca.* 0.05 Å shorter and *ca.* 0.09 Å longer, respectively, than the corresponding bonds in $[Ni(L^4 - H)]ClO_4$ ($L^4 - H$ = monodeprotonated L^4).[12] The large difference in the Ni–O distance of $[NiL^2]^{2+}$ and $[Ni(L^4 - H)]^+$ may be due in part to the fact that in the former two neutral hydroxyl groups are co-ordinated to the metal whereas one neutral and one deprotonated hydroxyl group are co-ordinated in the latter. However, another factor affecting the long Ni–O distance of $[NiL^2]^{2+}$, compared to $[Ni(L^4 - H)]^+$, may be the stronger in-plane Ni–N interactions. The short Ni–N distance of the complex of L^2, compared to that of $L^4 - H$, is consistent with the generally observed trend that substitution of secondary nitrogen atoms by tertiary ones in a 14-membered tetraaza macrocyclic complex lengthens the Ni–N distances.[17,22] The N–Ni–N angles of the five-membered chelate rings are, as expected, less than 90°, whereas those of the six-membered chelate rings are greater than 90°. Also, the O–Ni bond is not perpendicular to the NiN_4 plane with O(1)–Ni–N(1) and O(1)–Ni–N(2) angles of 79.9(2) and 87.2(1)°, respectively.

Spectra and Properties of the Complexes.—The complexes $[NiL^2][ClO_4]_2$ and $[CuL^2][ClO_4]_2$ are stable in the solid state and are soluble in polar solvents such as water, acetonitrile and nitromethane. The infrared spectra of the complexes show both ν(N–H) of the co-ordinated secondary amino groups and ν(O–H) of the pendant arms at *ca.* 3240 and 3360 cm^{-1}, respectively. The values of the molar conductances for the complexes measured in water (200–230 Ω^{-1} cm^2 mol^{-1}) and acetonitrile (240–280 Ω^{-1} cm^2 mol^{-1}) indicate that the complexes are 1 : 2 electrolytes.

The magnetic moment of $[NiL^2][ClO_4]_2$ in the solid state is 2.78 μ_B at 20 °C, which is consistent with a d^8 electronic configuration in octahedral geometry. Visible spectra (Table 4) of the nickel(II) complex in various solvents show d–d bands at 330 and 520 nm, indicating that the metal ion is in an octahedral environment. However, the wavelengths of the bands are much shorter than those found for $[NiL^4][ClO_4]_2$[12] indicating that the ligand-field strength of the octahedral complex is largely affected by the equatorial Ni–N interactions rather than the axial Ni–O interactions. The visible spectrum of a Nujol mull of $[CuL^2][CO_4]_2$ shows a d–d band at *ca.* 530 nm. The spectra of the copper(II) complex in various solvents shows this band at *ca.* 525 nm, which is *ca.* 120 nm shorter than that of $[CuL^4]^{2+}$ which was suggested to be a six-co-ordinated complex.[12] The spectrum of $[CuL^2]^{2+}$ is rather similar to those of square-planar copper(II) complexes of di-*N*-alkylated 14-membered tetraaza macrocycles such as L^5 (525 nm).[17,23] In the infrared spectrum of $[CuL^2][ClO_4]_2$ no splitting of the perchlorate band at 1100 cm^{-1} was observed. These results strongly indicate that the hydroxyethyl groups or perchlorate ions of the copper(II) complex are not co-ordinated to the metal ion in solution or in the solid state, in contrast to the corresponding nickel(II) complex.

In order to investigate the effects of the *N*-hydroxyethyl pendant arms on the redox properties of the nickel(II) and copper(II) complexes, the potentials *vs.* saturated calomel electrode (SCE) for the M^{II}–M^{III} and M^{II}–M^I processes were measured in acetonitrile solutions by cyclic voltammetry. Table 5 shows that the redox potentials for $[NiL^2]^{2+}$ are slightly more positive than those for $[NiL^1]^{2+}$. This is consistent with the generally observed trend that substitution of secondary amino groups by tertiary ones in a 14-membered tetraaza macrocyclic complex makes oxidation more difficult and reduction easier.[14,22–24] However, the oxidation potential for $[NiL^2]^{2+}$ is distinctly less positive than that for $[NiL^5]^{2+}$ [23] containing two *N*-ethyl pendant arms. This can be attributed to the co-ordination of the pendant hydroxyethyl groups; it has been noted that when pendant arms of a macrocyclic nickel(II) complex are co-ordinated to the metal ion the attainment of nickel(III) is made easier.[12,14] For $[CuL^2]^{2+}$, the reduction potential is quite similar to that of $[CuL^5]^{2+}$. Moreover, the oxidation potential is even slightly higher than that for the complex of L^5. This, together with the spectral data, clearly shows that the oxygen atoms of the $[CuL^2]^{2+}$ are not directly involved in co-ordination.

Kinetic Behaviour.—In order to investigate the effects of the hydroxyethyl pendant arms on the complex-formation reaction, a kinetic study was carried out. Pseudo-first order rate constants (k) for the complex formation of Cu^{2+} with L^1 and L^2 were obtained (see Experimental section) in sodium acetate buffer solutions (pH 5.4). (It is likely that the predominant forms of L^1 and L^2 involved in the reactions at pH 5.4 are the diprotonated species $[H_2L^1]^{2+}$ (ref. 25) and $[H_2L^2]^{2+}$, respectively.)[12,13] It was found that k (*ca.* 1.67×10^{-4} s^{-1}) for L^2 is much lower than that for L^1 (7.2×10^{-2} s^{-1}) under the same conditions. Interestingly, this result contradicts the reported trend that the reaction rates of fully *N*-functionalized macrocycles such as L^4 are much faster than those of the unfunctionalized macrocycles; for instance, the macrocycle L^4 instantaneously reacts with Cu^{2+} in aqueous solution, whereas L^3 reacts slowly.[11,12] It was assumed that the hydroxyethyl groups of L^4 promote the reaction by providing the points of the attachment outside the ligand for the metal ion. The reasons for the increased inertness of L^2, compared to L^1, are not clear at this time. However, it may be considered that, for L^2, the promoting effect of the hydroxyethyl groups is more than counterbalanced by the steric hindrance of the hydroxyethyl groups and the *C*-substituents. Unfortunately, we could not obtain the pseudo-first order rate constant for the complex formation of Ni^{2+} with L^2 under conditions similar to that for the copper(II) complex, because the absorption of $[NiL^2]^{2+}$ in the visible region is weak and is obscured by the bands of the added nickel(II) salt and/or buffer.

The copper(II) and nickel(II) complexes of L^2 are decomposed very slowly even in concentrated acid solutions; electronic spectra of $[CuL^2]^{2+}$ (1.0×10^{-3} mol dm^{-3}) in 0.3 mol dm^{-3} $HClO_4$ showed that $< 3\%$ of the complex was decomposed in 30 h at 25 °C. This behaviour is very similar to that observed for the complexes of unfunctionalized macrocycles such as L^1 (ref. 18) and L^5 (ref. 22) but is quite different from that observed for the complex of L^4. It has been reported that the half-life of $[CuL^4]^{2+}$ in 0.05 mol dm^{-3} $HClO_4$ is only 3.5 s at 25 °C, whereas $[CuL^3]^{2+}$ is not decomposed in 6 mol dm^{-3} HCl over a period of several weeks.[12]

Conclusion

This work has shown that the di-*N*-hydroxyethylated macrocycle L^2 can be easily obtained in high yield by the one-step reaction of L^1 with $BrCH_2CH_2OH$. The oxygen atoms of the pendant arms in $[NiL^2][ClO_4]_2$ are co-ordinated to the metal ion, whereas those in $[CuL^2][ClO_4]_2$ are not. This work also shows that the *N*-hydroxyethylation of L^1 to give L^2 scarcely affects the dissociation rate of the nickel(II) and copper(II) complexes in acidic solution and, moreover, reduces the rate of formation of the copper(II) complex unlike the case for the full *N*-hydroxyethylation of L^3 to give L^4.

Table 5 Cyclic voltammetric data for the nickel(II) and copper(II) complexes[a]

	E/V *vs.* SCE	
Complex	M^{II}–M^{III}	M^{II}–M^{I}
$[NiL^1]^{2+}$ [b]	+1.08	−1.28
$[NiL^2]^{2+}$	+1.14	−1.13(i)[c]
$[NiL^5]^{2+}$ [d]	+1.27	−1.08(i)
$[CuL^1]^{2+}$ [b]	+1.41	−0.92(i)
$[CuL^2]^{2+}$	+1.68(i)	−0.73(i)
$[CuL^5]^{2+}$ [d]	+1.60(i)	−0.74(i)

[a] Measured in 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ acetonitrile solution at 20 °C. [b] Ref. 18. [c] i = Irreversible. [d] Ref. 23.

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