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CO_2 fixation and activation by metal complexes of small polyazacyclophanes[†]

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ABSTRACT: The interaction of the cyclophanes 2,6,9,13-tetraaza[14]paracyclophane (**L1**) and 2,6,9,13-tetraaza[14]metacyclophane (**L2**) and of their Zn^{2+} and Cu^{2+} complexes with CO_3^{2-} and its protonated forms is described. The actuation of the Cu^{2+}–**L2** system as an electrocatalyst for the reduction of CO_2 to CO in water is advanced. Copyright © 2001 John Wiley & Sons, Ltd.
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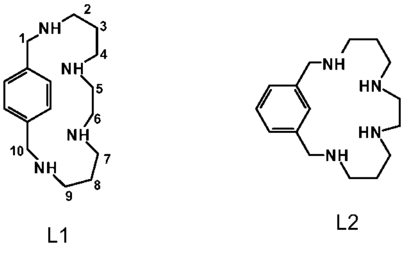
KEYWORDS: azacyclophanes; carbon dioxide; Cu^{2+} coordination; Zn^{2+} coordination; electrocatalysis

INTRODUCTION

Low-cost utilization of CO_2 to prepare organic chemicals has been a challenge for chemists in recent decades.[1] In order to convert the thermodynamically stable and relatively unreactive CO_2 molecule into desired products in an efficient manner, different molecular electrochemical or photochemical catalysts have been developed. Among them, the molecular complex $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) seems to be one of the most efficient electrocatalysts since, apart from achieving high catalytic activity, it is selective with respect to the reduction of water to hydrogen and, therefore, the process can be even carried out in aqueous solution.[2]

Recently, we synthesized and studied the metal ion coordination capabilities of a series of azacyclophane ligands characterized by the presence of a single aromatic unit linked to the ends of polyamine bridges with different numbers of nitrogen atoms and hydrocarbon chains between them. These topological features strongly influenced the chemistry of these compounds. Thus, for instance, the cyclophane 2,6,9,13-tetraaza[14]paracyclophane (**L1**) coordinates metal ions such as Cu^{2+}, Zn^{2+} or Hg^{2+} through just three out its four nitrogen atoms; the aromatic moiety, incorporated in the macrocyclic framework, prevents the full involvement of all its four nitrogens in the coordination to a single metal ion.[3] Therefore, the coordination spheres of the metal ions are not saturated by the nitrogen donors of the receptor and, thereby, can bind additional ligands.[4] One such ligand could be CO_3^{2-} in either its free or protonated form. This unsaturated coordination environment is a common feature in many Zn^{2+} and Cu^{2+} metalloenzymes.[5]



To check this point, we undertook a study on the interaction of the Cu^{2+} and Zn^{2+} complexes of the receptors **L1** and 2,6,9,13-tetraaza[14]metacyclophane (**L2**) with carbonate in aqueous solution. The formation of carbonate complexes was studied by potentiometry, and in the case of the Zn^{2+} complexes also by ^1H and ^{13}C NMR spectroscopy. Additionally, we tested the capabil-

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Table 1. Protonation constants of receptors **L1**[3] and **L2** determined in 0.15 M $NaClO_4$ at 298.1 K

Reaction[a]	**L1**[b]	**L2**[b]
$H + L = HL$	9.93(3)[b]	10.02(1)
$H + HL = H_2L$	9.09(1)	9.22(1)
$H + H_2L = H_3L$	7.43(1)	7.53(1)
$H + H_3L = H_4L$	3.61(1)	3.43(2)

[a] Charges omitted for clarity.
[b] Values in parentheses are standard deviations in the last significant figure.

Table 3. Equilibrium constants for the systems **L1**–CO_3^{2-} and **L2**–CO_3^{2-} ($A = CO_3^{2-}$) determined in 0.15 M $NaClO_4$ at 298.1 K

Reaction[a]	**L1**[b]	**L2**[b]
$L + A + H = HLA$	13.22(1)	13.33(1)
$L + A + 2H = H_2LA$	23.01(2)	23.28(2)
$L + A + 3H = H_3LA$	31.11(1)	32.04(2)
$HL + A = HLA$	3.29	3.31
$L + HA = HLA$	3.53	3.64
$HL + HA = H_2LA$	3.39	3.57
$H_2L + HA = H_3LA$	2.4	3.11

[a] Charges omitted for clarity.
[b] Values in parentheses are standard deviations in the last significant figure.

ities of the Cu^{2+} and Zn^{2+} complexes in the reduction of CO_2.[6] In aqueous media, carbon dioxide undergoes electrochemical reduction at highly negative potentials for which typical reduction products are carbon monoxide and formate and oxalate ions.[7]

RESULTS AND DISCUSSION

The protonation constants for **L2** determined potentiometrically at 298.1 K in 0.15 M $NaClO_4$ are shown in Table 1. For comparison, the constants of **L1** taken from the literature[3] are also included in Table 1. As can be seen, the replacement of a *para*- by a *meta*-substituted aromatic spacer is not accompanied by significant variations in the basicity constants. As determined by NMR, the protonation sequence follows similar trends to those reported for **L1**. The first two protonation steps affect mainly the benzylic nitrogen atoms and the fourth one occurs on the central nitrogens.[8]

In Table 2 are given the stability constants for the formation of Cu^{2+} and Zn^{2+} complexes under the same experimental conditions. The behavior previously described for the protonation can also be extended to the formation of metal complexes. The same speciation and similar values of the equilibrium constants are obtained for the *para*- and *meta*-substituted ligands. Therefore, it seems clear that also in the case of **L2** the presence of the aromatic spacer prevents the simultaneous coordination of both benzylic nitrogen atoms to a single metal ion. Molecular modeling calculations on **L2** support this point and show that the distance between the benzylic nitrogens is ~6.6 Å, a value that is not very different from that calculated for **L1** (6.9 Å). Accordingly, the ML^{2+} complexes display large protonation constants and the coordination sphere of the metal ions can be completed by additional exogenous ligands. As can be seen in the table, the formation of hydroxylated complexes is very important at high pH values for both Zn^{2+} and Cu^{2+} complexes.

The interaction of **L1** and **L2** and their metal complexes with CO_3^{2-} was also studied by potentiometry and the results are presented in Table 3. Potentiometric measurements show that the free receptor is able to interact with CO_3^{2-} anions in the pH range 11–7. Below this pH value, the measurements could not be followed owing to CO_2 evolution that altered the stability of the e.m.f. readings. In this pH range, for both receptors, the species $[HL(CO_3)]^-$, $[H_2L(CO_3)]$ and $[H_3L(CO_3)]^+$ were detected, with association constants varying between 2 and 4 logarithmic units. Addition of either Cu^{2+} or Zn^{2+} to form the ternary systems metal ion–receptor–carbonate yield a clear enhancement of the percentage of complexed carbonate (see Fig. 1 for the systems **L1**–CO_3^{2-}, Cu^{2+}–**L1**–CO_3^{2-} and Zn^{2+}–**L1**–CO_3^{2-}). Interestingly, in the presence of the metal ions there is a significant diminution of the pH at which CO_2 is liberated.

The potentiometric measurements allowed the identification of the species $[CuH\mathbf{L}(CO_3)]^+$, $[Cu\mathbf{L}(CO_3)]$ and

Table 2. Cu^{2+} and Zn^{2+} complex formation constants of receptors **L1**[3] and **L2** determined in 0.15 M $NaClO_4$ at 298.1 K

	L1[b]		**L2**[b]	
Reaction[a]	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
$M + L = ML$	13.01(1)[b]	6.83(1)	13.22(2)	8.73(2)
$ML + H = MHL$	7.80(1)	7.74(2)	8.18(1)	7.03(5)
$ML + H_2O = ML(OH) + H$	−9.10(1)	−8.67(2)	−10.06(2)	−8.01(2)

[a] Charges omitted for clarity.
[b] Values in parentheses are standard deviations in the last significant figure.

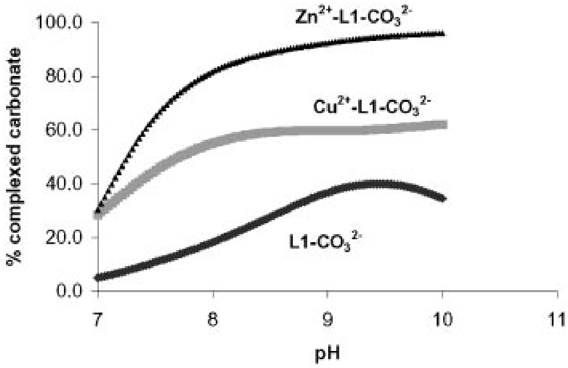


Figure 1. Plots of the percentage of complexed carbonate vs pH

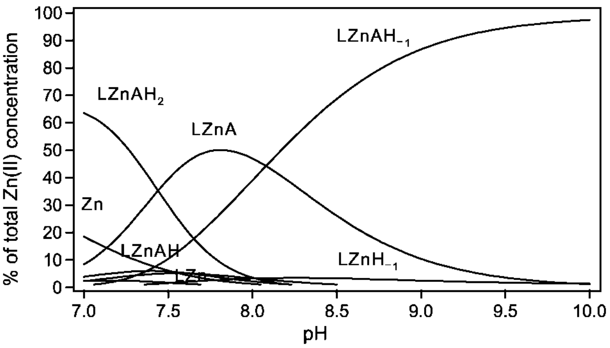
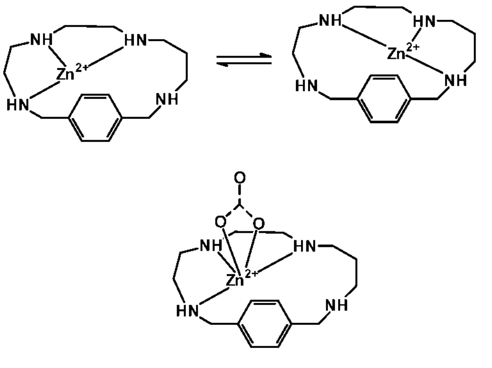


Figure 2. Distribution diagrams for the system Zn^{2+}–**L2**–CO_3^{2-} (Zn–L–A). concentration of all reactants, 1×10^{-3} M

$[Cu\mathbf{L}(OH)(CO_3)]^-$ for the Cu^{2+}–**L** systems and $[ZnH_2\mathbf{L}(CO_3)]^{2+}$, $[ZnH\mathbf{L}(CO_3)]^+$, $[Zn\mathbf{L}(CO_3)]$ and $[Zn\mathbf{L}(OH)(CO_3)]^-$ for the Zn^{2+}–**L** systems. The stability constants associated with these interactions are fairly high (Table 4); as an example, the constants for the equilibria $CuL^{2+} + CO_3^{2-} \rightleftharpoons CuL(CO_3)$ would be Cu^{2+}–**L1**, log$K = 4.26(3)$ and Cu^{2+}–**L2**, log$K = 4.61(5)$. The distribution diagram for the ternary system Zn^{2+}–**L2**–CO_3^{2-} is shown in Fig. 2.

Although coordination of the metal ions by three of the four nitrogen donors in the macrocycle should yield completely asymmetric complexes, this is not observed in the ^1H and ^{13}C NMR spectra in D_2O solutions. This is due to the broad signals that appear as a consequence of the metal coordination exchange between both sides of the macrocycle on the NMR scale-time (see Scheme **1**).[3,9] However, addition of a slight excess of carbonate yields a completely asymmetric spectrum with as many signals as there are carbon atoms in the macrocycle. Additionally, the signals become narrower owing to the fact that carbonate coordination slows the exchange process of the metal ion between the two equivalent parts of the molecule (see Scheme **1** and Fig. 3 for the system Zn^{2+}–**L1**–CO_3^{2-}). Indeed, in the NMR spectra with excess of carbonate both signals corresponding to free and complexed ligand can be observed (Fig. 3), as confirmed by assignment from 2D NMR correlation experiments (see Supplementary Material). Raman spectroscopy supports bidentate coordination of CO_3^{2-}. For solutions of the ternary complexes at pH 9.0, a signal at 1038 cm^{-1} [ν_2(A1)] attributable to this form of coordination appears.[10]



Scheme 1

Water-soluble Cu^{2+}–**L2** and Zn^{2+}–**L2** complexes catalyze the electrochemical reduction of CO_2, as indicated by voltammetric and coulometric experiments. In acidic media, cathodic linear scan voltammograms and differential pulse voltammograms of Cu^{2+}–**L2** complexes exhibit a single wave close to −0.25 V vs SCE, as shown in Fig. 4(A) and (B) for a solution at pH 5.3. In the subsequent anodic scan a classical stripping peak is recorded at +0.10 V, denoting the formation of metallic

Table 4. Equilibrium constants for the systems M^{2+}–**L1**–CO_3^{2-} and M^{2+}–**L2**–CO_3^{2-} ($M^{2+} = Cu^{2+}$ or Zn^{2+}) ($A = CO_3^{2-}$) determined in 0.15 M $NaClO_4$ at 298.1 K

	L1[b]		L2[b]	
Reaction[a]	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
$M + L + A + 2H = MH_2LA$				30.63(2)
$M + L + A + H = MHLA$	26.43(2)	21.32(1)	27.14(2)	22.42(2)
$M + L + A = MLA$	17.27(2)	13.29(2)	17.58(1)	15.75(1)
$M + L + A + H_2O = MLA(OH)$	7.67(1)	4.69(1)	—	7.67(2)

[a] Charges omitted for clarity.
[b] Values in parentheses are standard deviations in the last significant figure.

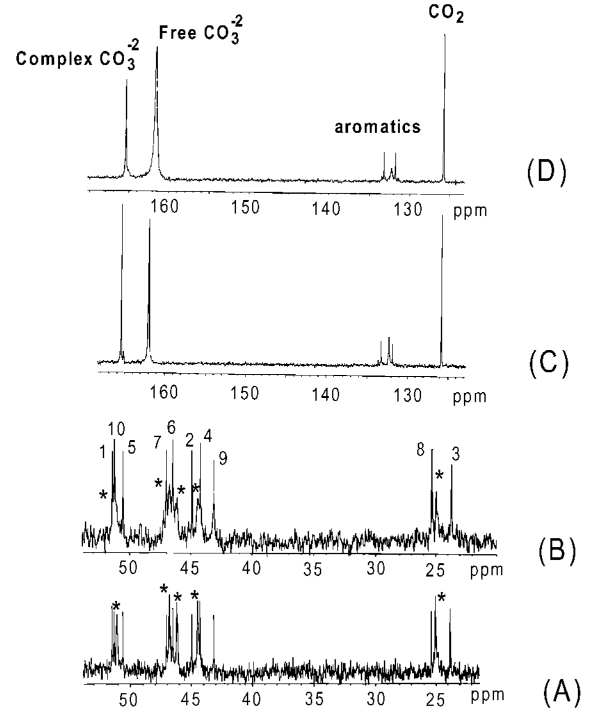


Figure 3. ^{13}C NMR spectra for Zn^{2+}–**L1**–$CO_3{}^{2-}$ solutions at pH 7: (A) 1:1:1 molar ratio, aliphatic region; (B) 1:1:3 molar ratio, aliphatic region; (C) 1:1:1 molar ratio, aromatic region; (D) 1:1:3 molar ratio, aromatic region. Asterisks correspond to the free ligand resonances

copper on the electrode surface during the prior cathodic step. In a CO_2-saturated solution at pH 5.3, linear scan and differential pulse voltammograms show two cathodic peaks at −0.36 and −0.50 V, as depicted in Fig. 4(C) and (D). A similar response is observed in neutral and alkaline media, suggesting the stabilization of the intermediate oxidation state Cu^+ towards its disproportionation into Cu^{2+} and Cu^0.

Cyclic voltammograms at pH 5.5 of Zn^{2+}, Zn^{2+}–**L2** and CO_2-saturated Zn^{2+}–**L2** solutions exhibit only one cathodic wave at −0.45, −0.74 and −1.07 V, respectively. The electrochemical pattern suggests that the electron-transfer process is preceded by dissociation of complex species. Then, the large cathodic shift of the reduction wave observed for ternary Zn^{2+}–**L2**–$CO_3{}^{2-}$ adducts reflects the larger stability of the mixed complexes with respect to the binary Zn^{2+}–**L2** one.

Linear scan voltammetric curves at a glassy carbon electrode (geometrical area 0.28 cm^2) for a CO_2-saturated aqueous solution in the absence and in the presence of Cu^{2+}–**L2** complexes, both at pH 5.3, are shown in Fig. 5. In the absence of the complex, a poorly defined cathodic wave appears at −1.34 V vs SCE preceding the proton discharge wave close to −1.7 V. In the presence of the Cu^{2+}–**L2** complex, only one prominent rising curve appears at less negative potentials. The peak intensity shows an 1800-fold increase with respect to that observed in the absence of the catalyst.

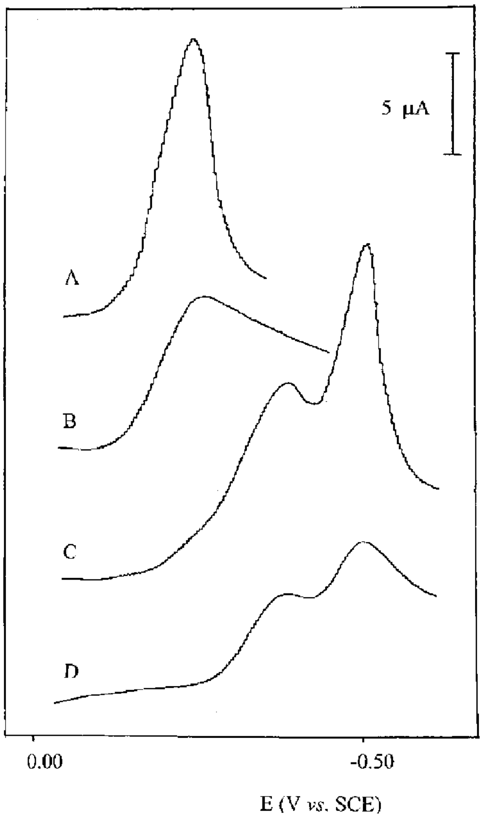


Figure 4. Cathodic differential pulse voltammograms (A, C) and linear scan voltammograms (B, D) at the glassy carbon electrode A, B: Cu^{2+}–**L2** (6×10^{-4} M); (C, D) the same solution CO_2-saturated. A, C: DPVs at $v = 10$ mV/s, DU = 80 mV C; D: LSVs at $v = 10$ mV/s. I = 0.15 M $NaClO_4$, pH = 5.25

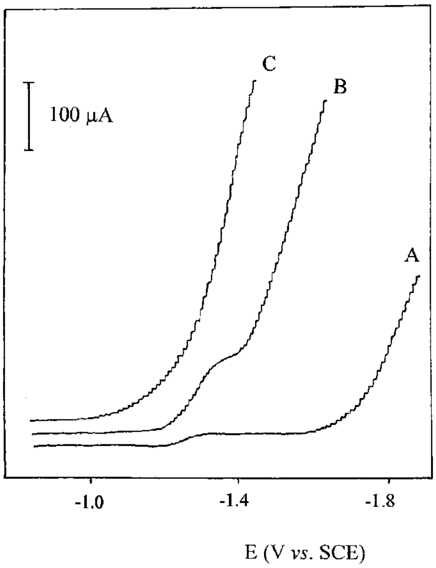


Figure 5. Cathodic linear scan voltammograms at the GCE for (A) CO_2-saturated solution (0.15 M $NaClO_4$); (B) the same plus Zn^{2+}–**L2** (0.50×10^{-3} M); (C) the same plus Cu^{2+}–**L2** (0.5010^{-3} M). pH 5.25; potential scan rate, 10 mV s^{-1}

In order to examine the kinetics of the process by which the copper complexes catalyse the electroreduction of carbon dioxide, it is instructive to carry out the reduction at rotating disk electrodes. The Levich plot of the plateau currents vs the square root of the rotation rate (included in the Supplementary Material) shows that the experimental points deviate from linearity as the rotation rate increases and such values are intermediate between the estimated responses for the diffusion–convection-controlled reduction of carbon dioxide by one ($n = 1$) or two ($n = 2$) electrons.

The corresponding Koutecky–Levich plot of (plateau current)$^{-1}$ vs electrode (rotation rate)$^{-1/2}$ is linear. The reciprocal of the intercept of this linear representation defines a potential-independent kinetic current, i_k, whose values increase linearly with the concentration of copper complex. These results indicate that the current-limiting reaction is first order with respect CO_2 and first order with respect the catalyst. In contrast, the values of i_k do not exhibit significant variations with the pH at a constant Cu^{2+}–**L2** concentration, denoting that the rate-limiting step is independent of pH. The catalytic effect, however, is largely confined to the pH range 3.5–6.5 and decreases drastically for pH >7.0. This effect is attributable to a compromise between the presence in the solution of significant amounts of complexed copper (requiring pH >3.5) and dissolved CO_2 (requiring pH <7.0).

It should be noted that the reduction of carbon dioxide at inert electrodes proceeds through the mechanism suggested by Amatore and Saveant[11] in which carbon monoxide, carbonate and oxalate ions can be formed through disproportionation or dimerization of the anion radical produced in the initial one-electron reduction of carbon dioxide. Subsequent one-electron transfer yields formate ions.

Since the catalytic reduction potential of CO_2 is considerably more negative than the formal reduction potential of the catalyst, it is likely that CO_2 reduction occurs at a potential corresponding to the redox potential of an adduct formed between the reduced substrate and the catalyst in agreement with the literature.[12]

This appears to be confirmed by voltammetric experiments after the potential was held at -1.0 V for a few minutes and then reasuming the scan. When the potential is switched beyond -1.50 V and scanned back, a crossover appears in the cyclic voltammograms (see Supplementray Material). This crossover is characteristic of the formation, at the electrode surface, of a product that is itself reducible at a potential just negative of the carbon dioxide reduction process.[13]

As discussed by Ley and Anson[14] for the catalytic effect of Cu^{2+}–phenanthroline complexes adsorbed on graphite electrodes on the electroreduction of dioxygen, a simple outer-sphere electron transfer between the Cu^{+}–**L2** complex and carbon dioxide is not likely because no reduction of CO_2 occurs at potentials near the formal potentials of the Cu^{2+}–**L2**/Cu^{+}–**L2** couple. Thus, an inner-sphere pathway involving the formation of ternary Cu^{+}–**L2**–CO_2 complexes seems called for. The large stability of ternary Cu^{+} complexes compared with that of Cu^{+}–**L2** binary complexes towards disproportionation and the first-order dependence of the kinetic currents calculated from Koutecky–Levich plots on the concentration of Cu^{2+}–**L2** suggests that the formation of such Cu^{+} intermediates plays a crucial role in the catalytic mechanism.

The electrocatalytic effect of Zn^{2+}–**L2** complexes is less intense than that of Cu^{2+}–**L2** complexes. Thus, in a CO_2-saturated solution at pH 5.3, the cathodic wave for the reduction of CO_2 is about 10 times larger than that recorded in the absence of the complex. Electrocatalysis is constrained to pH values between 4.5 and 7.0 because of the almost entire dissociation of Zn^{2+}–**L2** complexes below pH 5.0 and the protonation equilibria of carbon dioxide. The maximum catalytic effect appears at pH close to 6.0. Compared with the Cu^{2+} complexes, the less pronounced catalytic effect of Zn^{2+}–**L2** complexes reflects the importance of the relative stability of the intermediate Cu^{+} complex species.

EXPERIMENTAL

Materials. The synthesis of **L1** was accomplished following the general procedure reported elsewhere.[15] **L2** was prepared by a similar procedure and its synthesis will be published elsewhere. The compounds were handled as tetra(hydrobromide) salts and gave satisfactory elemental analyses and spectroscopic characterization. Data for **L2**.4HBr: m.p. 240–242 °C; ^{1}H NMR, solvent D_2O, δ_H (ppm) 1.90–2.05 (m, 4H), 3.01–3.18 (m, 8H), 3.40 (s, 4H), 4.29 (s, 4H), 7.47 (s, 3H), 7.62 (s, H); ^{13}C NMR, δ_C (ppm) 22.6, 42.3, 43.9, 44.7, 50.9, 131.5, 131.6, 132.8, 133.9. Anal. Calcd for $C_{16}H_{32}Br_4N_4$: C 32.03, H 5.38, N 9.34. Found: C 32.2, H 5.4, N 9.5%.

NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 300 and 400 spectrometers. The chemical shifts are reported in ppm from TMS but were measured against the solvent signal; dioxane ($\delta = 67.4$ ppm) was used as reference for ^{13}C NMR spectra in D_2O. All assignments have been performed on the basis of ^{1}H–^{13}C heteronuclear multiple quantum coherence experiments (HMQC, HMBC, GHMQC and GHMBC). The pH was calculated from the measured pD values using the correlation pH = pD -0.4.[16]

Potentiometric measurements. Stability constants were determined by pH-metry at 298.1 ± 0.1 K in 0.15 M $NaClO_4$ using the equipment that has been described elsewhere.[17] The program SUPERQUAD was used to establish the speciation of the system and to calculate the stability constants.[18] Measurements of the systems containing carbonate were usually run between pH 11 and ~7. Lower values of pH could not be explored owing to CO_2 evolution.

Raman spectroscopy. Spectra were recorded in an FT Raman Perkin-Elmer diode-pumped Nd:YAG laser PSU spectrometer. A total of 100 scans were measured at 960 mW.

Electrochemical experiments. Linear scan, cyclic and differential pulse voltammetric experiments for the Cu^{2+}–and Zn^{2+}–**L2** systems were performed on aqueous (0.15 M $NaClO_4$) solutions of Cu^{2+} or Zn^{2+} nitrates in the 10^{-6}–10^{-3} M concentration range, containing a stoichiometric amount or a small excess of the macrocyclic ligand. The solution was first degassed with argon and then cyclic voltammograms were recorded. Subsequently, CO_2 was bubbled in the solution over a period of 15 min and then voltammetric experiments were performed under a CO_2 atmosphere.

Solutions of the Cu^{2+} or Zn^{2+} complexes ions were prepared by mixing $Cu(NO_3)_2$ or $Zn(NO_3)_2$ with **L2** in a molar ratio of 1:1 in 0.15 M $NaClO_4$. The pH was adjusted to the required values by adding appropriate amounts of $HClO_4$ and/or NaOH solution.

Cyclic voltammetry was performed with a Newtronics 200P wave generator, an HQ101 potentiostat and a Riken-Denshi F35 *x–y* recorder. Linear scan and differential pulse voltammograms at stationary and rotating disk electrodes were obtained with a Metrohm E506 polarecord stand. Experiments were carried out in a conventional three-compartment cell with glassy carbon and gold working electrodes. A saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode completed the three-electrode configuration. Rotating disk voltammograms were obtained with a Metrohm 628-10 rotating disk device using a gold electrode (area 0.071 cm^2).

Prior to the series of experiments, the working electrode was cleaned and activated. Electrochemical pretreatment was performed in blank solutions by applying +1.50 V vs SCE for 10 min followed by −1.0 V for 1 min. Before each run the electrodes were polished with an aqueous suspension of alumina on a soft surface, dried and cleaned. Bulk electrolyses were performed in a two-electrode configuration using a two-arm voltammeter with pyrolytic graphite electrodes. All voltammetric experiments were performed at 25 °C under either an argon or a carbon dioxide atmosphere. A very slow flow of carbon dioxide was maintained during electrochemical measurements.

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