5540 *Inorg. Chem.* **1996,** *35,* 5540−5548

CO_2 Fixation by Novel Copper(II) and Zinc(II) Macrocyclic Complexes. A Solution and Solid State Study

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Received April 1, 1996[⊗]

Solutions containing Zn(II) and Cu(II) complexes with $[15]aneN_3O_2$ rapidly adsorb atmospheric CO_2 to give $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**2**) and $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**4**) complexes. The crystal structures of both complexes have been solved (for **2**, space group $R3c$, a, $b = 22.300(5)$ Å, $c = 17.980(8)$ Å, $V = 7743(4)$ Å^3, $Z = 6$, $R = 0.0666$, $R_w{}^2 = 0.1719$; for **4**, space group $R3c$, a, $b = 22.292(7)$ Å, $c = 10.096(8)$ Å, $V = 7788(5)$ Å^3, $Z = 6$, $R = 0.0598$, $R_w{}^2 = 0.1611$), and the spectromagnetic behavior of **4** has been studied. In both compounds a carbonate anion triply bridges three metal cations. Each metal is coordinated by one oxygen of the carbonate, three nitrogens, and an oxygen of the macrocycle; the latter donor weakly interacts with the metals. Although the two compounds are isomorphous, they are not isostructural, because the coordination geometries of Zn(II) in **2** and Cu(II) in **4** are different. The mixed complex $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ has been synthesized. X-ray analysis (space group $R3c$, a, $b = 22.323(7)$ Å, $c = 17.989(9)$ Å, $V = 7763(5)$ Å^3, $Z = 6$, $R = 0.0477$, $R_w{}^2 = 0.1371$) and EPR measurements are in accord with a μ_3-carbonate bridging one Cu(II) and two Zn(II) ions in $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}^{4+}$. Both the Zn(II) and Cu(II) cations exhibit the same coordination sphere, almost equal to that found in the trinuclear Zn(II) complex **2**. The systems Zn(II)/**L** and Cu(II)/**L** have been studied by means of potentiometric measurements in 0.15 mol dm^{-1} NaCl and in 0.1 mol dm^{-3} $NaClO_4$ aqueous solutions; the species present in solution and their stability constants have been determined. In both systems $[M\mathbf{L}]^{2+}$ species and hydroxo complexes $[M(II)\mathbf{L}OH]^+$ (M = Zn, Cu) are present in solution. In the case of Cu(II), a $[Cu\mathbf{L}(OH)_2]$ complex is also found. The process of CO_2 fixation is due to the presence of such hydroxo-species, which can act as nucleophiles toward CO_2. In order to test the nucleophilic ability of the Zn(II) complexes, the kinetics of the promoted hydrolysis of *p*-nitrophenyl acetate has been studied. The $[Zn\mathbf{L}OH]^+$ complex promotes such a reaction, where the Zn(II)-bound OH^- acts as a nucleophile to the carbonyl carbon. The equilibrium constants for the addition of HCO_3^- and CO_3^{2-} to the $[Zn\mathbf{L}]^{2+}$ complex have been potentiometrically determined. Only $[M\mathbf{L}(HCO_3)]^+$ and $[M\mathbf{L}(CO_3)]$ species are found in aqueous solution. A mechanism for the formation of $\{[M\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ is suggested.

Introduction

Over the years a great deal of interest has been focused on the role of metal ions in the active centers of hydrolytic metalloenzymes (*e.g.*, phosphatase, carboxypepdidase, carbonic anhydrase).[1] In alkaline phosphatase a zinc-bound water molecule plays a fundamental role in the hydrolytic mechanism, which involves the nucleophilic attack of a hydroxide anion to the phosphorous center, with the subsequent cleavage of the P−O bond.[1a,2] In carbonic anhydrases (CA) a zinc(II) hydroxide unit acts as nucleophile in the hydration of CO_2.[3] In CA the active site of the enzyme consists of a zinc center coordinated to three histidine imidazole groups and a water molecule in a distorted tetrahedral environment. The initial stages of the catalytic cycle are considered to involve initial deprotonation of the coordinated water to give the active zinc hydroxide derivative $[His_3Zn\text{-}OH]^+$, followed by reaction with CO_2 to give a zinc bicarbonate derivative $[His_3Zn\text{-}OCO_2H]^+$. In $[His_3Zn\text{-}OH]^+$ the arrangement of the donors, together with an adjacent imidazole and a hydrophobic environment around the Zn(II) ion, determines the considerably high acidity of the metal coordinated water molecule (pK_a, *ca.* 7).

As one of the approaches adopted to resolve the nature of the active site, a variety of Zn(II) complexes with synthetic receptors has been recently used as model systems for the above

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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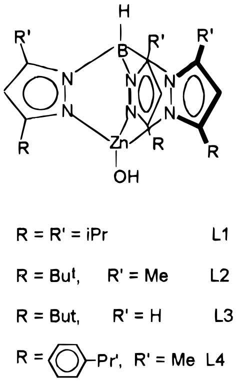
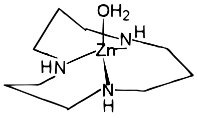
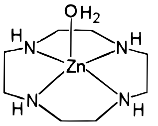
S0020-1669(96)00326-6 CCC: $12.00

enzyme.[4−11] Several zinc(II) pyrazolyl−borate complexes (**L1**−**L4**) containing a tetrahedral Zn(II)−OH unit are active in CO_2 fixation and hydrolysis of activated esters or phosphate esters.[10,11] The catalytic activity in such reactions rests in a strongly nucleophilic Zn−OH function, which is due to the electron-donating properties of the ligand which enhance the nucleophilicity of the coordinated hydroxide.





Zn(II)-[12]aneN$_3$



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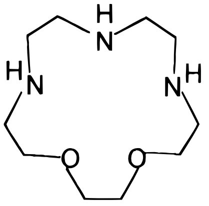

[15]aneN$_3$O$_2$

Moreover, the presence of a hydrophobic environment of the zinc hydroxide unit can further increase its nucleophilicity.[10d] The main deficiencies of these systems as CA models are the absence of the equilibrium which involves water deprotonation and scarce water solubility. Zn(II) macrocyclic complexes of various macrocyclic triamine and tetraamine ligands have been nicely studied by Kimura and co-workers as potential candidates for catalysis in CO_2 hydration and hydrolysis of activated esters or phosphate esters in water solution.[9] In these complexes the metal is coordinated to three or four amine groups and a water molecule, which can dissociate giving a Zn−OH function. The nucleophilicity of the zinc hydroxide unit is related to the pK_a of the coordinated water, and among the N_3 systems, the less stable macrocyclic complexes yield lower pK_a values.[9a]

The Zn^{II}−[12]aneN_3 complex can be considered the most successful model system for CA: the pK_a of the coordinated water molecule is close to that of CA, and the generated [12]aneN_3−Zn^{II}−OH species acts as nucleophile in CA-catalyzing reactions, such as in hydrolysis of activated ester.[9]

In the course of studies on enzyme mimicking by using Cu(II) and Zn(II) complexes with oxa−aza macrocycles as potential receptors for anionic substrates,[12] we have now analyzed the coordination features of the macrocyclic ligand [15]aneN_3O_2 (**L**). This ligand presents a N_3 binding unit linked to a rather hydrophobic polyethereal moiety.

Since ethereal oxygens in aqueous solution have weak coordinative ability toward Cu^{2+} and Zn^{2+},[13] it is expected that low-coordinated aquo− or hydroxo−metal complexes can be obtained. Thus, the Zn(II)−**L** complex is a potential model system for CA, and it can be of interest to investigate the effects of the rather hydrophobic polyethereal moiety on both the pK_a of the coordinated water molecule and the nucleophilicity of the related Zn−OH function.

We have already presented a few details regarding CO_2 fixation by solutions containing Cu(II) and Zn(II) complexes with **L** to form $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ and $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ compounds.[14]

In this paper we report the synthesis and the structural characterization of these compounds and the spectromagnetic behavior of the Cu(II) complex. The synthesis and characterization of the mixed complex $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ is also reported. Aiming to investigate the role played by the Cu^{II}−**L** and Zn^{II}−**L** systems in CO_2 hydration, we have analyzed, as a test for the nucleofilicity of the Zn−**L** complex, the hydrolysis of *p*-nitrophenyl acetate promoted by such a complex as well as the coordination behavior in aqueous solution of the $[Zn\mathbf{L}]^{2+}$ species toward HCO_3^- and CO_3^{2-}.

Experimental Section

General Methods. UV spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. ^{1}H NMR 200.0 MHz spectra were recorded at 298 K in a Bruker AC-200 spectrometer. Peak positions are reported relative to TMS (MeOD) or HOD at 4.75 ppm (D_2O). ESI mass spectra have been recorded on a TSQ 700 Finnigan mat apparatus. All reagents and solvents used were of analytical grade. 4-Nitrophenyl acetate was recrystallized from diethyl ether.

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Table 1. Crystal Data and Structure Refinement for $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**2**), $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**4**), and $\{[CuZn_2\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**5**)

	2	**4**	**5**
empirical formula	$C_{31}H_{69}Cl_4N_9O_{25}Zn_3$	$C_{31}H_{69}Cl_4N_9O_{25}Cu_3$	$C_{31}H_{69}Cl_4N_9O_{25}CuZn_2$
fw	1305.86	1300.37	1304.05
temp, K	298	298	298
wavelength, Å	0.710 69	0.710 69	0.710 69
space group	*R*3*c*	*R*3*c*	*R*3*c*
a, *b*, Å	22.300(5)	22.292(7)	22.323(7)
c, Å	17.980(8)	18.096(8)	17.989(9)
V, Å	7743(4)	7788(5)	7763(5)
Z	6	6	6
dens (calcd), mg/m^3	1.680	1.664	1.674
abs coeff, mm^{-1}	1.680	1.513	1.623
cryst size, mm	0.03 × 0.2 × 0.25	0.2 x 0.34 × 0.5	0.25 × 0.35 × 0.40
R^a $[I > 2\sigma(I)]$	0.0666	0.0598	0.048
$R_w{}^2\,b$	0.1719	0.1611	0.1371
a, *b*	0.0873, 57.92	0.1134, 29.01	0.0891, 16.32

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w{}^2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

Synthesis of the Compounds. 1,4-Dioxa-7,10,13-triazacyclopentadecane (**L**) was prepared as previously described.[15]

(a) $[Zn\mathbf{L}](ClO_4)_2\cdot H_2O$ (1). A solution of $Zn(ClO_4)_2\cdot 6H_2O$ (21 mg, 0.054 mmol) in CO_2-free methanol (5 cm^3) was added under nitrogen to a CO_2-free methanolic solution (5 cm^3) of **L** (12 mg, 0.054 mmol). Butanol (10 cm^3) was added to this solution. The complex was obtained as colorless powder by slow evaporation of the solvent under nitrogen (12.5 mg, 38%) Anal. Calcd for $C_{10}H_{25}N_3Cl_2O_{11}Zn$: C, 24.04; H, 5.04; N, 8.41. Found: C, 24.0; H, 5.2; N, 8.5. MS (ESI) (*m*/*z*): 380 ($Zn\mathbf{L}ClO_4{}^+$), 140.5 ($Zn\mathbf{L}^{2+}$), 280 ($Zn\mathbf{L}ClO_4{}^+ - HClO_4$). The same product can be obtained by slow evaporation under nitrogen of CO_2-free aqueous solutions containing **L** and $Zn(ClO_4)_2$ in equimolecular ratio.

(b) $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$. (2) A CO_2-free 0.05 mol dm^{-3} aqueous solution of $Zn(ClO_4)_2\cdot 6H_2O$ was added to an equimolecular aqueous solution of **L**. The solution was adjusted to pH 9.5 with the addition of NaOH. Air was bubbled through the resulting solution. After 15 min colorless crystals of the complex were formed (63% yield). Anal. Calcd for $C_{31}H_{69}Cl_4N_9O_{25}Zn_3$: C, 28.51; H, 5.32; N, 9.65. Found: C, 28.6; H, 5.3; N, 9.7. MS (ESI) (*m*/*z*): 281 ($Zn\mathbf{L} + H^+$), 141 ($Zn\mathbf{L}^{2+}$).

By bubbling air through CO_2-free methanolic solutions containing $Zn(ClO_4)_2\cdot 6H_2O$ and **L** (both the final concentrations 0.025 mol dm^{-3}) in the presence of 1 equiv of NaOH, the product **2** was isolated in higher yield (78%). Crystals suitable for X-ray analysis with the same crystallographic cells were obtained from both solvents.

(c) $[Cu\mathbf{L}](ClO_4)_2\cdot H_2O$ (3). This compound was synthesized from $Cu(ClO_4)_2\cdot 6H_2O$ (20 mg, 0.054 mol) and **L** (12 mg, 0.054 mol) following the procedure reported for **1**, obtaining **3**, as a blue solid (14.7 mg, 45% yield). Anal. Calcd for $C_{10}H_{25}N_3Cl_2O_{11}Cu$: C, 24.22; H, 5.08; N, 8.48. Found: C, 24.3; H, 5.2; N, 8.5. MS (ESI) (*m*/*z*): 379 ($Cu\mathbf{L}ClO_4{}^+$), 140 ($Cu\mathbf{L}^{2+}$), 279 ($Cu\mathbf{L}ClO_4{}^+ - HClO_4$).

(d) $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (4). This compound was synthesized from $Cu(ClO_4)_2\cdot 6H_2O$ and **L** following the procedure reported for **2**, obtaining **4** as a blue solid (59% yield). The same reaction can also be performed in methanol (73% yield). Crystals suitable for X-ray analysis with the same crystallographic cells were obtained from both solvents. Anal. Calcd for $C_{31}H_{69}Cl_4Cu_3N_9O_{25}Cu_3$: C, 28.63; H, 5.34; N, 9.69. Found: C, 28.8; H, 5.4; N, 9.7. MS (ESI) (*m*/*z*): 279 ($Cu\mathbf{L} + H^+$), 140 ($Cu\mathbf{L}^{2+}$).

(e) $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (5). A CO_2-free aqueous solution (20 cm^3) containing $Zn(ClO_4)_2\cdot 6H_2O$ (33.6 mg, 0.09 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (3.7 mg, 0.01 mmol) was added to a CO_2-free aqueous solution of **L** (21.7 mg, 0.1 mmol). The pH was adjusted at 9.5 with NaOH, and the resulting solution was placed aside in contact with the atmosphere. After 1 h the pale blue crystals formed were filtered off (8.2 mg, 65% yield). Anal. Calcd for $C_{31}H_{69}Cl_4Cu_3N_9O_{25}CuZn_2$: C, 28.55; H, 5.33; N, 9.66; Cu, 4.87; Zn, 10.03. Found: C, 28.6; H, 5.4; N, 9.6; Cu 4.9; Zn 10.1. Further atmospheric exposure of the resulting solution led to crystallization of compound **2**.

X-ray Structure Analysis. Analyses on a prismatic colorless single crystal of $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**2**), a prismatic blue crystal of $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**4**), and a pale blue crystal of $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**5**) were carried out with an Enraf-Nonius CAD4 X-ray diffractometer which uses an equatorial geometry, with graphite monochromated Mo Kα radiation. A summary of the crystallographic data is reported in Table 1.

Cell parameters for all compounds were determined by least-squares refinement of diffractometer setting angles for 25 carefully centered reflections. The intensities of two standard reflections per compounds were monitored during data collections to check the stability of the diffractometer and of the crystal; no loss of intensity was recognized.

A total of 1583 and 1592 reflections was collected for **2** and **4**, respectively, up to $2\theta = 50°$. For **5**, 2327 reflections were collected, up to $2\theta = 56°$. Intensity data were corrected for Lorentz and polarization effects, and an absorption correction was applied once the structures were solved by the Walker and Stuart method.[16]

These structures were solved by the heavy atom technique, which showed the metal centers for all compounds. Remaining non-hydrogen atoms were found by means of subsequent Fourier maps. Refinements were performed by means of the full-matrix least-squares method of SHELXL-93[17] programs which uses the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all atoms from ref 18. The function minimized was $\sum w(F_o{}^2 - F_c{}^2)^2$ with $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ and $P = (F_o{}^2 + 2F_c{}^2)/3$, where *a* and *b* are adjustable parameters (their final values are reported in Table 1).

(a) $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (2). Crystals of this compound belong to the rhombohedral family, space group *R*3*c* ($Z = 6$), and lattice constants *a*, *b* = 22.300(5) Å, *c* = 17.980(8) Å. The zinc, chlorine, nitrogen, and oxygen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were introduced in calculated positions, and their coordinates were refined in agreement with those of the linked atoms, with an overall thermal parameter refined up to a final value of 0.09(1) $Å^2$. For 176 refined parameters the final agreement factors were $R = 0.067$ and $R_w{}^2 = 0.17$ for 1236 observed reflections with $I > 2\sigma(I)$.

(b) $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (4). Crystals of this compound belong to the rhombohedral family, space group *R*3*c* ($Z = 6$), and lattice constants *a*, *b* = 22.292(7) Å, *c* = 18.096(8) Å. The copper, chlorine, nitrogen, and oxygen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were introduced in calculated positions and their coordinates refined in agreement with those of the linked atoms, with an overall temperature factor refined up to 0.096(7) $Å^2$. Two different models were found for the C10 and C11 carbon atoms, which were introduced by using population parameters 0.5. For

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175 refined parameters the final agreement factors were $R = 0.060$. $R_w{}^2 = 0.16$ for 1423 observed reflections with $I > 2\sigma(I)$.

(c) {[CuZn$_2$L$_3$](μ_3-CO$_3$)}·(ClO$_4$)$_4$ (5). The compound is isomorphous with **2**, being the lattice constants $a = b = 22.323(7)$ Å and $c = 17.989(9)$ Å. Anisotropic temperature factors were used for the nonhydrogen atoms. All of the hydrogen atoms were introduced in calculated positions with an overall isotropic temperature factor refined to 0.103(9) Å^2. The positional parameters of the hydrogens bound to the carbon atoms were varied accordingly to these ones, while the hydrogens of the secondary nitrogens were not refined. Zinc and copper atoms were introduced with identical coordinates and temperature factors which were kept equal during the refinement. According to the stoichiometry of the compound, the occupation factors of the copper and zinc ions were fixed to 0.66 and 0.33, respectively; any attempt to refine them results in very high estimated standard deviations. The final agreement factors were $R = 0.048$ and $R_w{}^2 = 0.1371$ for 227 refined parameters and 1971 reflections having $I > 2\sigma(I)$.

Magnetic and EPR Measurements. Temperature variation of the magnetic susceptibility of {[Cu**L**]$_3$(μ_3-CO$_3$)}·(ClO$_4$)$_4$ was measured in the temperature range 3−210 K using a Metronique Ingegnierie Super Conducting Quantum Interference Device magnetometer on a sample with mass 24.43 mg. A diamagnetic correction of -663×10^{-6} cm^3 mol^{-1} was applied to the measured data.

Electron paramagnetic resonance spectra were measured with a Varian E-9 spectrometer equipped with an Oxford Instrument continuous flow cryostat in the temperature range 4.2−300 K on polycrystalline powders.

Kinetics of 4-Nitrophenyl Acetate Hydrolysis. The hydrolysis rate of 4-nitrophenyl acetate in aqueous solution was measured by an initial slope method following the increase in the 403 nm absorption of the released 4-nitrophenolate. The ionic strength was adjusted to 0.15 with NaCl. The reaction solution was maintained at 25 ± 0.1 °C. MOPS (pH 7−7.8) , TAPS (pH 7.8−8.9), and CHES (pH 9.1) buffers were used (50 mM). In a typical experiment, after 4-nitrophenyl acetate and Zn(II)−**L** (0.1−1 mM) in 10% CH_3CN solution at appropriate pH (the reference experiment does not contain the Zn(II) complex) were mixed, the UV absorption decay was recorded immediately and was followed generally until 2% decay of 4-nitrophenyl acetate. A plot of the hydrolysis rate vs [total Zn(II)] concentration (0.1−1 mM) at a given pH gave a straight line, and then we determined the slope/[*p*-nitrophenyl acetate] as the second order rate constants k'_{np} (M^{-1} s^{-1}). Errors on the k'_{np} values were about 10%. In order to compare the Zn−**L** activity with that of the Zn(II) complex with [12]aneN$_3$, k'_{np} was also determined at pH 8.2 in 0.1 mol dm^{-3} NaClO$_4$.

Emf Measurements. All potentiometric measurements were carried out in 0.15 mol dm^{-3} NaCl or in 0.1 mol dm^{-3} NaClO$_4$ aqueous solution at 298.1 ± 0.1 K, by using the equipment which has been already described.[19] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO$_2$-free NaOH solutions and determining the equivalent point by the Gran method,[20] which allows one to determine the standard potential $E°$, and the ionic product of water (pK_w = 13.73 at 298.1 ± 0.1 K). Titrations for the determination of the ligand basicity constants and Zn(II) and Cu(II) complexation constants were performed, in the pH range 2.5−10, by using CO$_2$-free aqueous solutions containing ligand and metal ion in 10^{-3} mol dm^{-3} concentrations. These systems were studied both in 0.15 mol dm^{-3} NaCl and in 0.1 mol dm^{-3} NaClO$_4$. In order to evaluate the interaction of Cl$^-$ with [Cu**L**]$^{2+}$ and [Zn**L**]$^{2+}$ complexes, titrations were performed in the presence of NaCl with 30:1 Cl$^-$:Zn^{II} or Cl$^-$:Cu^{II} molar ratio in 0.1 mol dm^{-3} NaClO$_4$. No interaction with this anion was found.

Finally, the binding of CO$_3{}^{2-}$ to the metal complexes was studied in 0.15 mol dm^{-3} NaCl by titrating with standardized HCl solutions alkaline solution (pH 10) containing **L,** Zn(II), and Na$_2$CO$_3$ in 1:1:0.3, 1:1:0.6, and 1:1:1 molar ratios. In order to better estimate the formation constants of the Zn/**L**/carbonate and hydrogen carbonate complexes, measurements on solution containing Na$_2$CO$_3$ in excess (**L**:Zn^{II}:Na$_2$CO$_3$ from 1:1:1 to 1:1:5 molar ratios) were also carried out. The titrations were performed until pH 7 in order to avoid the equilibria involving CO$_2$ evolution. The protonation constants of CO$_3{}^{2-}$ and the formation constants for the carbonate complexes with Zn(II) were determined by separated measurements. The values obtained are equal within the experimental error to those already reported.[21]

At least three measurements were performed for each system (100 data points each measurement). The computer program SUPERQUAD[22] was used to calculate both protonation and stability constants from emf data. The titration curves for each system were treated either as a single set or as independent entities without significant variations in the values of the stability constants.

Results and Discussion

Complex Synthesis. The ligand **L** binds Cu(II) and Zn(II) in aqueous and methanolic solutions. Solid complexes [M**L**](ClO$_4$)$_2$·H$_2$O (M = Cu, Zn) can be isolated by slow evaporation under nitrogen of CO$_2$-free solutions containing **L** and Zn(ClO)$_4$ or Cu(ClO$_4$)$_2$ in equimolecular ratio.

Aqueous solutions of such complexes have a great affinity for atmospheric CO$_2$, readily extracting it from the air. By bubbling air through solutions in the pH range 8.5−10 (ligand and metal concentrations 0.025 mol dm^{-3}), CO$_2$ is rapidly adsorbed (15 min), forming the triply bridged carbonate complexes **2** and **4** in good yields. The same products can be also obtained simply by exposing alkaline aqueous solutions of the above metal complexes in the air. The time needed for crystallization depends on the concentration of the solutions and the surface extension exposed to the air. Finally, CO$_2$ uptake is also observed in methanolic solutions containing **L**, M(ClO$_4$)$_2$, and NaOH in equimolecular ratio. In this case crystals of **2** and **4** are obtained in even higher yields. While fixation of CO$_2$ by transition metal complexes is common, only a few examples of CO$_2$ uptake in air are reported.[11,23] In these cases the CO$_2$ fixation occurs in a few days or in some hours. The present complexes with **L** can trap carbon dioxide in a few tens of minutes, both in water and in methanolic solutions.

Since compounds **2** and **4** are isomorphous (*vide infra*), attempts to crystallize mixed complexes {[Cu$_x$Zn$_y$**L**]$_3$(μ_3-CO$_3$)}·(ClO$_4$)$_4$ were carried out. To this purpose, aqueous solutions containing Zn(ClO$_4$)$_2$ and Cu(ClO$_4$)$_2$ in different percentages were exposed to the air. Compound **5** crystallizes from solutions containing small amounts of Cu(II) (5−10%) in rather good yield. After its removal from the solution, further crystallization of pure compound **2** occurs. Complex **5** is isomorphous with compounds **2** and **4**. From solutions containing a higher Cu(II) percentage (70−95%) pure compound **4** firstly crystallizes. After its removal, colorless crystals of **2** are formed.

{[ZnL]$_3$(μ_3-CO$_3$)}·(ClO$_4$)$_4$ (2). The molecular structure of **2** consists of trinuclear complex cations {[Zn**L**]$_3$(μ_3-CO$_3$)}$^{4+}$ and perchlorate anions. Selected bond lengths and angles are listed in Table 2. The ORTEP[24] drawing of the cation (Figure 1a) shows the presence of μ_3-CO$_3{}^{2-}$ bridging the three metal ions through the three oxygens of the carbonate group. The complex cation possesses a 3-fold crystallographic symmetry axis, perpendicular to the plane containing the carbonate anion and passing through C1.

Each metal center, which lies 0.189(2) Å apart from the carbonate plane, is coordinated by the three nitrogens and the

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{[ZnL]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$

Zn−O1	1.946(8)	Zn−N2	2.185(13)
Zn−N3	2.100(12)	Zn−O9	2.337(10)
Zn−N1	2.127(12)	C1−O1	1.283(7)
O1−Zn−N3	115.5(4)	N1−Zn−N2	80.7(5)
O1−Zn−N1	121.1(4)	O1−Zn−O9	103.7(4)
N3−Zn−N1	123.0(5)	N3−Zn−O9	72.4(4)
O1−Zn−N2	102.5(4)	N1−Zn−O9	99.2(5)
N3−Zn−N2	81.8(5)	N2−Zn−O9	149.2(5)
O1−C1−O1′	119.99(4)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\{[CuL]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$

Cu−O1	1.935(7)	Cu−N2	2.058(11)
Cu−N1	1.989(10)	Cu−O9	2.531(13)
Cu−N3	2.034(10)	C1−O1	1.278(6)
O1−Cu−N1	168.9(4)	O9−Cu−N3	69.9(5)
O1−Cu−N3	99.1(3)	O8−Cu−O9	62.1(5)
N1−Cu−N3	83.8(5)	O1−Cu−O9	101.0(5)
O1−Cu−N2	90.4(4)	N1−Cu−O9	90.1(6)
N1−Cu−N2	83.2(5)	N2−Cu−O9	128.6(4)
N3−Cu−N2	157.3(5)	O1−C1−O1′	119.998(8)

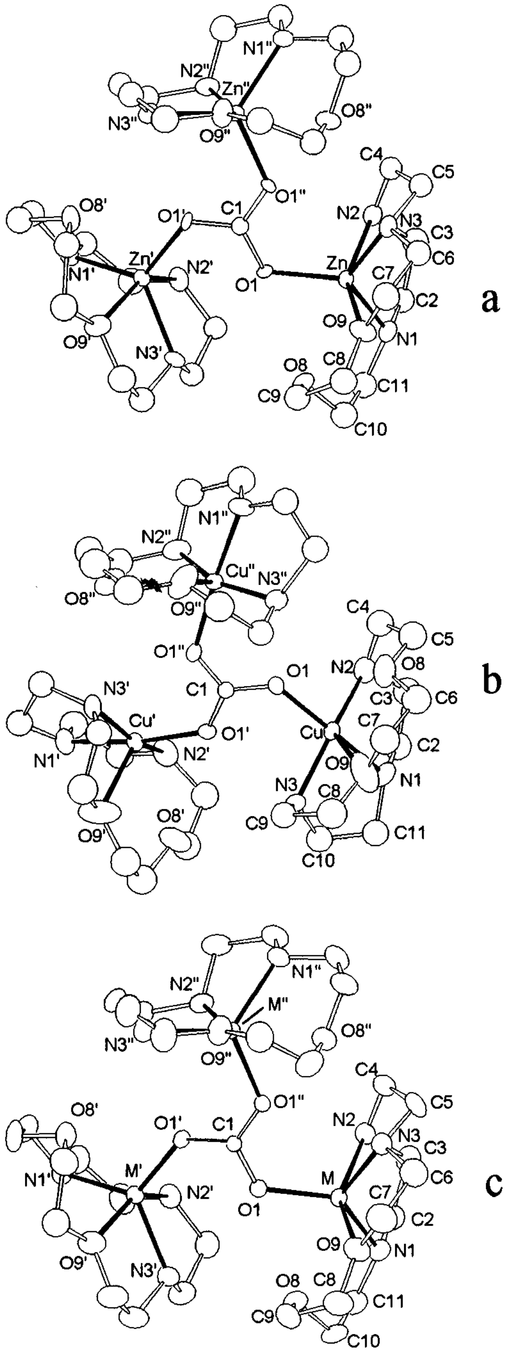

Figure 1. ORTEP drawings of the $\{[ZnL]_3(\mu_3\text{-}CO_3)\}^{4+}$ (a), $\{[CuL]_3(\mu_3\text{-}CO_3)\}^{4+}$ (b), and $\{[CuZn_2L_3](\mu_3\text{-}CO_3)\}^{4+}$ (c) cations. In c the copper and zinc atoms are indicated with M, according to the refinement procedure of this structure reported in the text.

O9 atom of the ligand and by the oxygen atom of the carbonate (O1). The geometrical arrangement of the donor atoms around the zinc atom results in a distorted trigonal bipyramid with N1, N3, and O1 lying on the equatorial plane and N2 and O9 occupying the axial position. The N2−Zn−O9 bond angle shows the maximum of deviation from the expected theoretical value (149.2(5)° *vs* 180°). The Zn−N and Zn−O1 bond lengths are in the range which is usually expected for this kind of compounds,[12,23a,25] while O9 is weakly bound to the metal (Zn−O9, 2.34 Å).

The macrocyclic framework assumes a folded conformation along the N2−O8 direction, with a dihedral angle of 112.6(4)° between the two mean planes defined by the ten-membered N2/O8 and the seven-membered O8/N2 chains.

$\{[CuL]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (4). This compound is isomorphous to **2**. The molecular structure is made up of $\{[CuL]_3(\mu_3\text{-}CO_3)\}^{4+}$ trinuclear complex cations (Figure 1b) and perchlorate anions. The complex possesses a 3-fold crystallographic symmetry axis passing through the carbon atom of the triply bridging carbonate ion (C1), with the three symmetry related metal centers shifted 0.294(1) Å from the carbonate plane.

Nevertheless, **2** and **4** are not isostructural, since the coordination sphere of the metals as well as the disposition of both the macrocycle and the carbonate are different in the two complexes.

The coordination environment of the Cu(II) in **4** can be described as a distorted square pyramid, with N1, N2, N3, and O1 at the vertices of the basal plane (maximum deviation, 0.12(1) Å for N2) and O9 in the apical position. Similar to **2**, the oxygen of the polyoxa chain (O9) is weakly bound to the metal (see Table 3). An angle of 61.6(4)° is formed between such a plane and the Cu−O9 bond direction. Finally, the copper atom is 0.243(1) Å apart from the basal plane.

In complex **4** the macrocyclic ligand **L** wraps around the Cu(II) ion in a different fashion than that observed in **2**. Such a different disposition can be visualized as a rotation around the M−O1 bond direction. As a consequence, N3 and O8 mutually exchange their position in the two complexes. Furthermore, the carbonate anion is rotated of *ca.* 60° around the 3-fold axis. The different disposition of both the macrocycle and CO_3^{2-} gives rise to the different coordination geometry observed for the two metal ions.

However, the overall conformation of the macrocyclic framework is not remarkably different in the two complexes, since in **4** the macrocycle adopts a folded conformation along the N2−N3 direction. The two mean planes, defined by the ten membered N2−N3 and the seven membered N3−N2 chains, form a dihedral angle of 103.6(5)°, which is similar to that found in **2**.

Similar coordinated carbonate has been rarely observed in Cu(II) complexes.[26] Aiming to further characterize such a complex, we have analyzed its spectromagnetic behavior.

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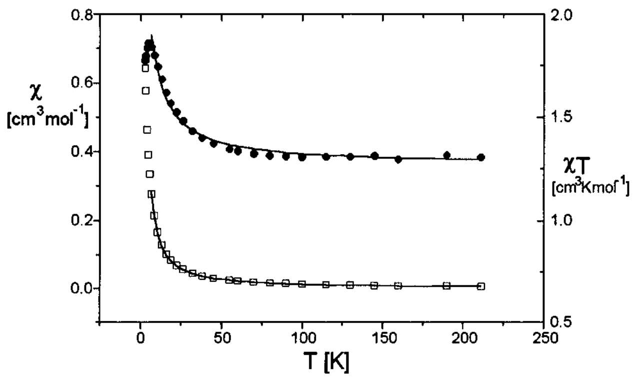

Figure 2. Temperature variation of the magnetic susceptibility of $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ in the form χ *vs* T (bottom, left *Y* axis) and χT *vs T* (top, right *Y* axis). Solid lines represent the best fit curves according to the procedure described in the text.

The temperature dependence of the magnetic susceptibility of $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ (**4**) measured in the range 3−210 K is shown in Figure 2 in the form χ *vs T* (bottom) and χT *vs T*. At temperatures higher than ~100 K the magnetic moment $\mu_{\text{eff}} = (8\chi T)^{1/2}$ reaches the constant value of 3.2 μ_B, which compares well with the value expected for three uncoupled spins $S = {}^1/_2$ ($\mu_{\text{eff}} = 3.0$ μ_B, spin only formula). Below 100 K the magnetic moment increases until a maximum between 4.0 and 5.0 K is reached. The increase of μ_{eff} can be ascribed to a ferromagnetic interaction between the Cu(II) centers. From this interaction, in fact, three spin states arise which correspond to the total spin $S = {}^1/_2$ (two states) and $S = {}^3/_2$. For a symmetric trinuclear species, like **4** in which the paramagnetic centers are related by a C_3 crystallographic axis, the two singlet states are degenerate, and the magnetic susceptibility[27] can be related to the population of the magnetic states using the simplified expression

$$\chi = \frac{Ng^2\mu_B^{\ 2}}{4kT}\,\frac{1 + 5e^{-3J/2kT}}{1 + e^{-3J/2KT}} \tag{1}$$

where *N* is the Avogadro number and *k* is the Boltzmann constant. In (1) *J*, the exchange coupling constant, is the energy difference between the high spin $S = {}^3/_2$ state and the two degenerate $S = {}^1/_2$ states. A negative value of *J* stabilizes the quartet states and indicates a ferromagnetic interaction. The magnetic data of **4** have been fitted to eq 1 using a Simplex minimization routine for temperatures higher than 6.0 K, using *J* as a free parameter. The value of *g* was fixed at 2.12 according to the EPR results which will be described later. The results of the fitting are graphically shown in Figure 2 as solid lines. The value of *J* obtained from the fit is $J = -8.2(6)$ cm^{-1}. Below 6 K the magnetic moment decreases. This effect cannot be accounted for by eq 1 and can be attributed to intercluster antiferromagnetic interactions.[27] The characterization of these interactions is outside the purpose of the present paper, and we have not attempted to reproduce them. The observed value of the ferromagnetic interaction compares well with that measured in $Na_2Cu(CO_3)_2$ (−8.2 cm^{-1}), which behaves as a three-dimensional ferromagnet.[28]

EPR spectra have been recorded on polycrystalline samples of **4** over the whole temperature range between 300 and 4.2 K. At any temperature only a single resonance was observed with linewidth ~ 150 G almost temperature independent. The *g* value was also found to be almost constant, varying from 2.103 to 2.116 on passing from room temperature to 4.2 K. The spectra are typical of exchange narrowed systems,[29] and no evidence of signals arising from the zero field splitting of the quartet state was found.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$[a]

M1−O1	1.950(4)	M1−N2	2.188(6)
M1−O9	2.329(6)	M1−N1	2.116(6)
M1−N3	2.113(7)	C1−O1	1.268(4)
O1−M1−N3	114.8(2)	N1−M1−N2	81.4(3)
O1−M1−O9	104.3(2)	O1−M1−N1	121.9(2)
N3−M1−O9	73.2(2)	N3−M1−N1	122.9(3)
N1−M1−O9	98.2(3)	O1−M1−N2	102.4(2)
N2−M1−O9	148.5(3)	N3−M1−N2	80.6(3)
O1−C1−O1′	120.000(4)		

[a] The copper and zinc atoms are indicated with M, according to the refinement procedure of the structure reported in the text.

$\{[Zn_2CuL_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$. The structure of this compound is almost identical to that found for **2** (see Table 4 and Figure 1c). On the other hand the elemental analysis indicates that the compound contains copper and zinc in 1:2 molar ratio. Because of the presence of a 3-fold crystallographic axis passing through the C1 atom of the carbonate anion, the trinuclear complex is affected by disorder. However, the thermal parameters of the metals and of the atoms of the macrocyclic framework well compare with those found for the zinc and copper analogous complexes. Therefore, we can deduce that the copper ion adopts the coordination environment of the zinc one. Such an adaptation of the metal ion in minor percentage to the crystal structure of the host metal complex is known.[30] It has been explained considering that the influence of the host lattice suffices to induce the "guest" metal complex to change its own structure in favor of that of the “host” metal complex.[30a]

In order to shed further light on the structure of **5,** polycrystalline powder EPR spectra have been recorded on this compound from room temperature to 4.2 K. At any temperature an intense signal attributable to an axial $S = {}^1/_2$ spin system was observed showing a well-resolved hyperfine interaction with a nuclear spin $I = {}^3/_2$ in the parallel region. The spin Hamiltonian parameters, read from the spectra at 4.2 K, are as follows: $g_{\|} = 2.23$, $g_{\perp} = 2.06$, $A_{\|} = 193 \times 10^{-4}$ cm^{-1}. The observed value of the hyperfine coupling compares well with the splitting observed in mononuclear Cu(II) complexes,[31] indicating that **5** does not contain dinuclear or trinuclear Cu(II) metal assemblies of the type $(ZnCu_2)(\mu_3\text{-}CO_3)$ or $(Cu_3)(\mu_3\text{-}CO_3)$. The observation of the hyperfine splitting indicates also that the paramagnetic centers are diluted in a diamagnetic host lattice.

Even if the X-ray analysis does not allow one to discriminate between Cu(II) and Zn(II) in the crystal lattice, the EPR data are in accord with the presence of mononuclear Cu(II) metal complexes only. These findings lead us to consider **5** as a trinuclear μ_3-carbonate $\{[CuZn_2\mathbf{L}_3](\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ complex with the carbonate ion bridging one Cu(II) and two Zn(II) cations.

Solution Studies. Aiming to get further information on the process of CO_2 fixation, the systems Cu(II)/**L** and Zn(II)/**L** have been studied by means of potentiometric measurements in aqueous solution. Table 5 collects the stability constants for

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Table 5. Logarithms of the Equilibrium Constants for the Formation of Cu^{2+} and Zn^{2+} Complexes with **L** Determined in 0.15 mol dm^{-3} NaCl and in 0.1 mol dm^{-3} $NaClO_4$ at 298.1 K

	Cu(II)		Zn(II)	
reaction	NaCl	$NaClO_4$	NaCl	$NaClO_4$
$M^{2+} + \mathbf{L} = [M\mathbf{L}]^{2+}$	15.51(2)[a]	15.65(2)	8.95(2)	9.03(3)
$[M\mathbf{L}]^{2+} + OH^- = [M\mathbf{L}OH]^+$	4.72(4)	4.77(4)	4.92(2)	4.93(3)
$[M\mathbf{L}OH]^+ + OH^- = [M\mathbf{L}(OH)_2]$	1.96(4)	2.02(4)		

[a] Values in parentheses are standard deviations on the last significant figure.

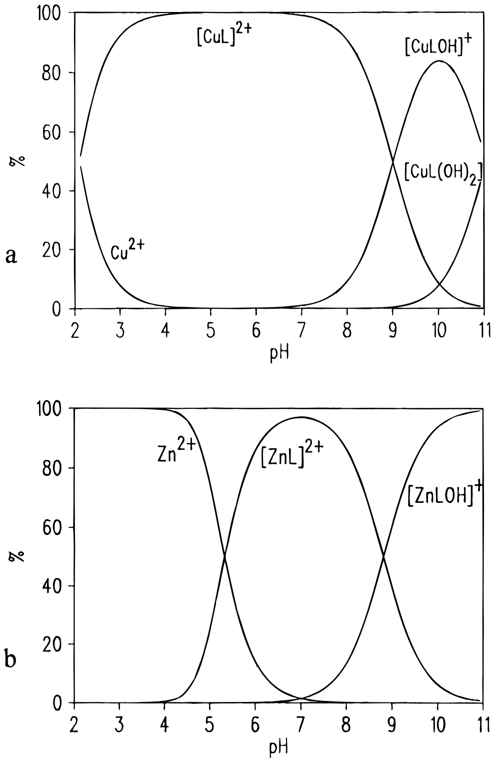

Figure 3. Distribution diagrams for the systems Cu(II)/**L** (a) and Zn(II)/**L** (b) (0.15 mol dm^{-3} NaCl aqueous solution, [**L**] = [M(II)] = 1 × 10^{-3} mol dm^{-3} (M = Cu, Zn)).

Table 6. Formation Constants (log *K*) for Zn(II) Complexes of Some Triamine and Tetraamine Macrocycles and pK_a of the Coordinated Water

	$Zn^{2+} + \mathbf{L}' = [Zn\mathbf{L}']^{2+}$	
$\mathbf{L}'$	log *K*	pK_a
[15]aneN_3O_2	8.95	8.81
[12]aneN_3	8.41[a]	7.30[a]
iso-[12]aneN_3	7.01[a]	7.34[a]
[11]aneN_3	10.41[b]	8.2[b]
[10]aneN_3	10.3[b]	
[9]aneN_3	10.3[b]	
[12]aneN_4	16.2[a]	8.02[a]
[14]aneN_4	15.5[a]	9.77[a]

[a] 0.1 mol dm^{-3} $NaClO_4$ aqueous solution, from ref 9a. [b] 0.1 mol dm^{-3} $NaNO_3$ aqueous solution, from ref 34.

the complexes of **L** with Cu(II) and Zn(II) potentiometrically determined in 0.15 mol dm^{-3} NaCl and in 0.1 mol dm^{-3} $NaClO_4$ aqueous solution at 298.1 K.[32]

In both systems, monohydroxo $[Zn\mathbf{L}OH]^+$ and $[Cu\mathbf{L}OH]^+$ species are present at alkaline pH (see Figure 3). In the case of Cu(II), a dihydroxo $[Cu\mathbf{L}(OH)_2]$ complex is also found. The stability constants are almost equal in the two ionic media.

Since the ethereal oxygens have weak coordinative ability toward such metal ions,[13,33] in the $[M\mathbf{L}]^{2+}$ complexes we may suppose that the metal is coordinated by the three nitrogens, while the polyoxa chains give a little contribution to the stability of such species. Although the crystal structures of compounds **2**, **4**, and **5** show that one oxygen of the polyoxa chain is involved in the coordination of Zn(II) and Cu(II), in both cases the M···O distances are indicative of a weak interaction between the metal and the oxygen atom. Table 6 collection of the stability constants for the Zn(II) complexes formed by **L** and other macrocyclic tri- and tetraamines, together with the pK_a values of the coordinated water molecule. Indeed, the thermodynamic stability of the $[Zn\mathbf{L}]^{2+}$ complex is similar or somewhat lower than those reported for triazamacrocycles and by far lower than those for tetraazamacrocycles; this observation confirms that in $[Zn\mathbf{L}]^{2+}$ the three nitrogens are involved in metal coordination, while the oxygens are unbound or, at most, poorly contribute to the stability of these complexes. As a consequence of the low coordination number, facile deprotonation of coordinated water molecules occurs, giving hydroxylated species.

The formation of $[M\mathbf{L}OH]^+$ species seems to play a fundamental role in the process of hydration and fixing of CO_2. Indeed, no formation of complexes **2** and **4** is observed even by atmospheric exposure for several days of aqueous solution at pH ≤ 7, where such hydroxo complexes are absent (see Figure 3). A similar behavior is found in methanol. Methanolic solutions containing $M(ClO_4)_2$ and **L** in 1:1 molar ratio do not adsorb CO_2, while, by adding 1 equiv of NaOH, crystallization of complex **2** or **4** readily occurs. It is of interest that the ^1H NMR spectra of a methanolic solution containing $Zn(ClO_4)_2$ and **L** is almost equal to that recorded in aqueous solution at neutral pH.[35] These spectra can be attributed to a $[Zn\mathbf{L}]^{2+}$ species which does not exhibit ability in CO_2 fixation. On the other hand the ^1H NMR spectrum recorded on a CO_2-free methanolic solution containing $Zn(ClO_4)_2$, **L**, and NaOH in equimolecular ratios shows analogous spectral features in comparison with those found for aqueous solution at pH 9.6, where the $[Zn\mathbf{L}OH]^+$ species is present in large amount. These observations point out that CO_2 fixation takes place only in the presence of hydroxo complexes in methanol also.

4-Nitrophenyl Acetate Hydrolysis. The ability of M−OH species in hydrolysis of activated esters has currently been used to evaluate the nucleophilicity of such hydroxo complexes. Furthermore, CA promote 4-nitrophenyl acetate hydrolysis.[36] In these enzymes second order kinetics is followed and involves the direct nucleophilic attack at the carbonyl group by a Zn−OH species.

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(32) Protonation constants of **L**: log K_1 = 9.44(1), log K_2 = 8.58(1), log K_3 = 1.52(2) (0.15 mol dm^{-3} NaCl aqueous solution); log K_1 = 9.64(1), log K_2 = 8.61(1), log K_3 = 2.43(2) (0.1 mol dm^{-3} $NaClO_4$ aqueous solution). $K_n = [\mathbf{L}H_n^{\,n+}]/[\mathbf{L}H_{(n-1)}^{\,(n-1)+}][H^+]$. Their values are in good accord with those found by Hancock et al.[15]

(33) (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721−2085. (b) Bradshaw, J. S. *Aza-Crown Macrocycles*; Wiley: New York, 1993.

(34) Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531−2536.

(35) The ^1H NMR spectrum of $[Zn\mathbf{L}]^{2+}$ (D_2O solution, pD 7) shows several sharp multiplets at 2.57 (m, 4H), 3.07 (m, 4H) (hydrogen atoms of the ethylenic chains linking two nitrogen atoms), 2.88 (m, 2H), 3.16 (m, 2H), 3.68 (m, 2H), 3.84 (m, 2H) (ethylenic chains linking a nitrogen and an oxygen), and 3.89 ppm (s, 4H) (ethylenic chains linking two oxygens). The spectrum recorded on a MeOD solution containing Zn(II) and **L** in equimolecular ratio is almost equal. By adding NaOH to the $[Zn\mathbf{L}]^{2+}$ aqueous solution a marked line broadening is observed. The spectrum recorded in D_2O solution at pD 10 ($[Zn\mathbf{L}OH]^+$) shows five broad signals at 2.58 (4H), 2.94 (4H) (hydrogen atoms of the ethylenic chains linking two nitrogen atoms), 3.00 (4H), 3.70 (4H) (ethylenic chains linking a nitrogen and an oxygen), and 3.80 ppm (s, 4H) (ethylenic chains linking two oxygens). The spectrum recorded on a MeOD solution containing Zn(II), **L**, and NaOH in equimolecular ratio shows analogous features with broad resonances at 2.67 (4H), 3.00 (4H), 3.05 (4H), 3.75 (4H), and 3.80 ppm (s, 4H).

(36) Pocker, Y.; Stone, J. T. *Biochemistry* **1967**, *6*, 668.

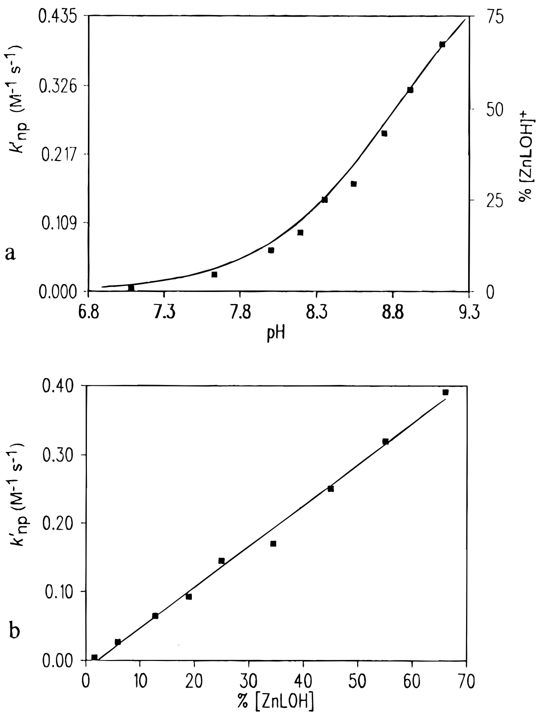

Figure 4. (a) Plot of the distribution curve of $[ZnLOH]^+$ (solid line, right *Y* axis) and k'_{np} values (■, left Y axis) as a function of pH (0.15 mol dm^{-3} NaCl). (b) Constants for promoted hydrolysis of *p*-nitrophenyl acetate by Zn−**L** (k'_{np}) as a function of $[Zn\mathbf{L}OH]^+$ percentage.

The Zn(II) complex with **L** promotes 4-nitrophenyl acetate hydrolysis, and second order rate constants k'_{np} have been determined at different pH values. In Figure 4a,b the k'_{np} values are reported as a function of pH and of $[Zn\mathbf{L}(OH)]^+$ concentration, respectively. Figure 4a shows that the k'_{np} values fit the distribution curve of the $[Zn\mathbf{L}(OH)]^+$ species. No effect is observed at pH < 7, where such hydroxo complex is absent in solution. Finally, the plot of the k'_{np} as a function of the concentration of $[Zn\mathbf{L}(OH)]^+$ gives rise to a straight line (Figure 4b).

These results point out that (i) $[Zn\mathbf{L}OH]^+$ is the kinetically active species, *i.e.*, this Zn(II)−OH species is indeed nucleophilic, and (ii) the hydrolysis of the ester occurs *via* a bimolecular mechanism, which would involve the nucleophilic attack of the metal-bound hydroxide to the carbonyl group of the ester and release of *p*-nitrophenate.

These findings are in accord with Kimura's work with Zn(II) complexes with tri- and tetraaza macrocycles.[9] Among these complexes, Zn^{II}−[12]aneN_3 has been considered as the best model system for CA.[9a] In particular, the pK_a of the coordinated water molecule, 7.3, is very close to that reported for CA (*ca.* 7).[3] The $[Zn([12]aneN_3)OH]^+$ complex has been completely characterized, the Zn(II) being coordinated by the three nitrogens and a hydroxide anion in a tetrahedral mode. It has been observed that, among the triaza macrocycle, the less stable zinc complexes yield lower pK_a values.[9a,33] The present $[Zn\mathbf{L}]^{2+}$ complex exhibits a lower acidity of the coordinated water molecule (p$K_a = 8.8$) in comparison with the Zn(II) complexes with triazamacrocycles (see Table 6). This is quite surprising since in $[Zn\mathbf{L}]^{2+}$ only three nitrogens are coordinated to the metal.

Recently we have reported that interactions *via* hydrogen bonds of metal-coordinated water molecules with the oxygens of polyoxa chains in oxa−aza macrocyclic complexes stabilize such aquo species, leading to a drastic reduction of the acidity of the M−OH_2 species.[37] In other words, the increased thermodynamic stability of the Zn−OH_2 species leads to an enhancement of the pK_a of the complex. In the light of these results, the formation of hydrogen bonds between the coordinated water of the Zn−OH_2 unit and the oxygens of the dioxa chain of the macrocycle may explain the rather high values found for the pK_a of the present Zn(II) complex.

As an effect of the higher pK_a of $[Zn\mathbf{L}]^{2+}$ with respect to the $[Zn([12]aneN_3)]^{2+}$ complex, the concentration of the active $[Zn\mathbf{L}OH]^+$ species is by far lower than the hydroxo species $[Zn([12]aneN_3)OH]^+$ at the same pH. Nevertheless, the present Zn(II)−**L** and Kimura's complex show very similar rate constants in *p*-nitrophenyl acetate hydrolysis. At pH 8.2 ($NaClO_4$, 0.1 mol dm^{-3}) $k'_{np} = 4.1 \times 10^{-2}$ M^{-1} s^{-1} for Kimura's complex[9a] and $k'_{np} = 5.1(2) \times 10^{-2}$ M^{-1} s^{-1} for the Zn−**L** complex.[38]

Second order rate constants k_{np} can be determined from the k'_{np} values as follows:

$$v = k'_{np}[\text{total Zn(II) complex}][p\text{-nitrophenyl acetate}] = k_{np}[Zn\mathbf{L}OH^+][p\text{-nitrophenyl acetate}]$$

Considering the different amounts at pH 8.2 of the two hydroxo complexes, the k_{np} values can be calculated in 5.2×10^{-2} M^{-1} s^{-1} for $[Zn([12]aneN_3)OH]^+$ and 25.5×10^{-2} M^{-1} s^{-1} for $[Zn\mathbf{L}OH]^+$. The reaction promoted by $[Zn\mathbf{L}OH]^+$ is almost five times faster than by $[Zn([12]aneN_3)OH]^+$.

It can be concluded that $[Zn\mathbf{L}OH]^+$ exhibits a stronger nucleophilic activity than $[Zn([12]aneN_3)OH]^+$. In other words, the presence of the polyoxa framework reduces the acidity of the coordinated water but increases the nucleophilicity of the Zn^{II}−OH function.

The increase in nucleophilicity of the Zn−OH unit in going from [12]aneN_3 to **L** cannot be related to the different electron releasing power of the chains linking the nitrogen donors, since the ethylenic groups are poorer σ-donors than propylenic ones. The observation that the $[Zn\mathbf{L}OH]^+$ complex is a better nucleophile in comparison with $[Zn([12]aneN_3)OH]^+$ may be related to steric effects due to the shorter ethylenic chains linking the nitrogens, which can produce a different coordination environment with respect to that almost tetrahedral one found in $[Zn([12]aneN_3)OH]^+$, as well as to solvation effects due to the presence of the polyethereal chain. Particularly, polyethereal moieties are poorly solvated in water. Thus, the presence of a dioxa chain within the cyclic framework can provide a rather hydrophobic environment for the Zn−OH unit, increasing its nucleophilic activity.

Carbonate Binding. In order to obtain further information on the formation of hydrogen carbonate and carbonate complexes, we performed the speciation of the systems Zn^{II}/**L**/CO_3^{2-}. The species formed by the Zn(II) metal complex with carbonate and hydrogen carbonate and the corresponding formation constants, potentiometrically determined in 0.15 mol dm^{-3} NaCl aqueous solution, are reported in Table 7. Figure 5 shows a distribution diagram of the species present in aqueous solution as a function of pH. This system cannot be studied in 0.1 mol dm^{-3} $NaClO_4$ since precipitation of compound **2** occurs in such a medium.

The titration curves for carbonate binding were analyzed by considering all of the possible species deriving from successive

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(37) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Fusi, V.; Paoletti, P.; Valtancoli, B. *J. Chem. Soc., Dalton Trans.* **1994**, 3581−3588.

(38) It is known that the rate of catalyzed hydrolysis of *p*-nitrophenyl acetate is influenced by the ionic medium used. Considering the case of our Zn−**L** complex, $k'_{np} = 5.1 \times 10^{-2}$ M^{-1} s^{-1} in 0.1 mol dm^{-3} $NaClO_4$ at pH 8.2, while $k'_{np} = 8.9 \times 10^{-2}$ M^{-1} s^{-1} at the same pH in 0.15 mol dm^{-3} NaCl. The rate increase in promoted hydrolysis of *p*-nitrophenyl acetate in NaCl with respect to $NaClO_4$ has been nicely discussed by: Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622−2636.

Table 7. Logarithms of the Equilibrium Constants for the Addition of HCO_3^-, CO_3^{2-}, and OH^- to the $[Zn\mathbf{L}]^{2+}$ Complex Determined in 0.15 mol dm^{-3} NaCl at 298.1 K

	log K [a]		
complex	HCO_3^-	CO_3^{2-}	OH^-
$[Zn\mathbf{L}]^{2+}$	2.2(1)	3.6(1)	4.92(2)
Zn^{II}−CA	1.6[c]		6.4[c]
$[Zn([12]aneN_3)]$	2.8[d]		6.5[e]

[a] $K = [Zn\mathbf{L}A]/[Zn\mathbf{L}][A]$, where A = HCO_3^-, CO_3^{2-}, and OH^-. [b] Values in parentheses are standard deviations on the last significant figure. [c] Determined by inhibition kinetics in CA-promoted *p*-nitrophenyl acetate hydrolysis at pH 8.2.[35] [d] From ref 9d. [e] From ref 9a.

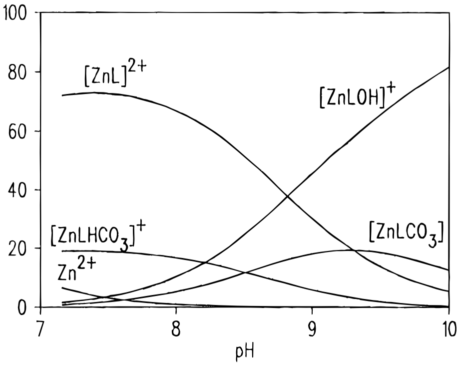
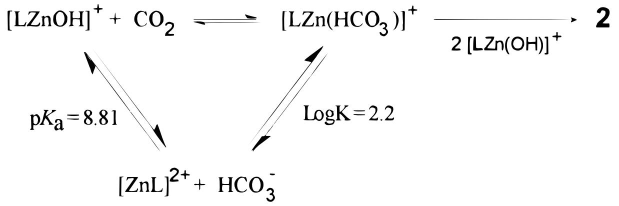


Figure 5. Distribution diagram for the system Zn(II)/**L**/carbonate (0.15 mol dm^{-3} NaCl aqueous solution, $[\mathbf{L}] = [M(II)] = [CO_3^{2-}] = 1 \times 10^{-3}$ mol dm^{-3}).

dissociations of the $\{[Zn\mathbf{L}]_3(\mu_3\text{-}CO_3)\}^{4+}$ complex found in the solid state. All fitting procedures were consistent with the formation of only $[Zn\mathbf{L}CO_3]$ and $[Zn\mathbf{L}HCO_3]^+$ species, *i.e.*, the concentration of polynuclear carbonate complexes is too low to be monitored. Attempts to isolate the mononuclear complex were performed by slow evaporation under nitrogen of such solutions. Due to its low solubility, however, the crystalline products that were isolated under these conditions were the trinuclear complex **2**.

It is remarkable that the order and the magnitude of the equilibrium constant for the addition of HCO_3^- to the $[Zn\mathbf{L}]^{2+}$ complex is similar to that reported for CA (log $K = 1.6$).[39] Furthermore, the presence of a hydrogen carbonate complex $[Zn\mathbf{L}HCO_3]^+$ in solution is interesting in that it can give information on the mechanism of CO_2 hydration. We propose that the metal-bound hydroxo ion acts as nucleophile and combines reversibly with CO_2, producing a hydrogen carbonate complex, $[Zn\mathbf{L}(HCO_3)]^+$. This complex equilibrates with $[Zn\mathbf{L}]^{2+}$ and HCO_3^-, with an equilibrium constant similar to that found for CA. HCO_3^- exhibits a much lower affinity to the Zn(II) complex than OH^- (log $K = 2.2$ *vs* 4.92, Table 7), indicating that the weaker binding hydrogen carbonate anion tends to be replaced by the stronger binding hydroxide anion.



Finally, a tentative mechanism for the formation of complexes **2** and **4** may be suggested looking at Figure 5, which shows a distribution diagram of the species present in solution containing Zn(II), **L**, and Na_2CO_3 in equimolecular ratio. It can be noted that in the pH range 7−10, where the formation of **2** takes place, both $[Zn\mathbf{L}(HCO_3)]^+$ and $[Zn\mathbf{L}OH]^+$ species are present in solution. It is reasonable to believe that the $[M\mathbf{L}(HCO_3)]^+$ complexes can react subsequently with $[M\mathbf{L}OH]^+$ species to form the **2** and **4** trinuclear complexes. The reactivity toward CO_2 of Zn(II) complexes with alkyl substituted tris(pyrazolyl)−hydroborato ligands gives us confidence about this hypothesis.[10] In fact, the hydroxo complex **L1** combines reversibly with CO_2 in apolar solvents (*e.g.*, benzene or toluene), giving rise to a hydrogen carbonate adduct which can further react with hydroxo species to form a μ-CO_3^{2-} dizinc complex.

Concluding Remarks. Both Zn(II) and Cu(II) complexes with **L** readily adsorb atmospheric CO_2, giving rise to $\{[M\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ complexes, both in water at alkaline pH and in methanolic solution. Both complexes are isomorphous and their molecular structures show the μ_3-CO_3^{2-} anion bridging the three metal ions through the three oxygens of the carbonate group. In $\{[Cu\mathbf{L}]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ the Cu(II) ions are weakly ferromagnetically coupled as previously observed in an analogous μ_3-bridged carbonate complex.[26] A long-range antiferromagnetic interaction between the trinuclear moieties prevents a more accurate measurement of the exchange coupling constant which is found to be ∼−8 cm^{-1}.

Few examples of CO_2 uptake in air are reported.[11,24] The CO_2 uptake by these M−**L** complexes is very fast in comparison with the previous metal complexes which can fix CO_2 from the air. The fixation is due to the presence in solution of $[M\mathbf{L}OH]^+$ species, which may act as nucleophiles toward CO_2, giving rise to $[M\mathbf{L}HCO_3]^+$ complexes. Further reaction with $[M\mathbf{L}OH]^+$ species forms the trinuclear complexes **2** and **4**, which are isolated in high yields due to their low solubility. The first step, *i.e.*, the reversible formation of a hydrogen carbonate adduct, which equilibrates with an aquo−Zn^{II} complex and HCO_3^-, resembles the mechanism currently accepted for hydration of CO_2 by CA. Furthermore, the constant for the equilibrium $[Zn\mathbf{L}]^{2+} + HCO_3^- = [Zn\mathbf{L}(HCO_3)]^+$ is similar to that found for CA.

The effective role of the $[Zn\mathbf{L}OH]^+$ species as a nucleophile has been confirmed by studies of promoted hydrolysis of *p*-nitrophenyl acetate. The second order kinetics and the plot of the rate constants *vs* the $[Zn\mathbf{L}OH]^+$concentration point to a reaction mechanism involving the direct nucleophilic attack of Zn^{II}−OH at the carbonyl carbon. Although these rates are much slower than those with CA, the reaction mechanism is the same as the one found in CA.

It can be concluded that this Zn^{II}−**L** complex provides an interesting model for studying the mechanism of CO_2 hydration by CA.

Acknowledgment. Financial support by Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (quota 60%) is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data, positional parameters, isotropic and anisotropic thermal factors, bond distances and angles (19 pages). Ordering information is given on any current masthead page.

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(39) (a) Lindskog, S.; Malmström, B. J. *J. Biol. Chem.* **1962**, 237, 1129−1137. (b) Coleman, J. E. *Nature* **1967**, *214*, 193−194. (c) Thorslund, A.; Lindskog, S. *Eur. J. Biochem.* **1967**, *3*, 117.