

Fixation of CO₂ by Zinc(II) Chelates in Alcoholic Medium. X-ray Structures of $\{[\text{Zn}(\text{cyclen})]_3(\mu_3\text{-CO}_3)\}(\text{ClO}_4)_4$ and $[\text{Zn}(\text{cyclen})\text{EtOH}](\text{ClO}_4)_2$

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Received November 14, 1996[⊗]

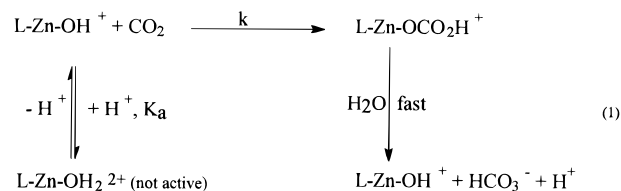
The fixation of CO₂ on Zn(II) chelates in alcoholic medium was studied in efforts to synthesize alkyl carbonates. In the presence of a base, such as NEt₃, the tetraazacyclododecane complex of Zn(II) in alcoholic solution binds CO₂ and forms a μ₃-carbonate complex. This complex was characterized by NMR spectroscopy and X-ray analysis. Crystal data: orthorhombic; space group *Pcba*; *a* = *b* = *c* = 21.850(5) Å; α = β = γ = 90°; *V* = 10431.7(6) Å³; *Z* = 8. The central Zn atom is coordinated to the four nitrogen donor atoms and to one oxygen of the bridging carbonate group. In an organic solvent such as DMSO, the complex exists in equilibrium with the decarboxylated Zn(II) complex. In addition, a Zn^{II}(cyclen)(ethanol) complex was isolated and characterized by X-ray analysis. Crystal data: monoclinic; space group *P2₁/n*; *a* = 12.707(5), *b* = 11.780(5), *c* = 15.642(5) Å; α = γ = 90°; β = 105.250(5)°; *V* = 2259.0 (6) Å³; *Z* = 4. The central Zn atom is coordinated to four nitrogen donor atoms and the oxygen of ethanol. We were not successful in converting this complex to the ethyl carbonate complex. The results of this study are discussed in reference to those published in the literature.

Introduction

There has been a long-standing interest in the fixation and activation of CO₂ for the conversion of CO₂ to various carbonates, formic acid, and other stock chemicals.^{1–6} In recent years, supercritical CO₂ has become a popular, environmental friendly (clean chemistry) reaction medium, under which conditions the medium can also be activated to participate as a reaction partner.^{7–9} These developments have stimulated research efforts in various fields dealing with the activation and conversion of CO₂.

One such area has dealt with the spontaneous and catalyzed hydration of CO₂ and dehydration of HCO₃[–] in aqueous solution, in which the focus fell on the important role of Zn(II) in the catalytic mechanism of carbonic anhydrases and model Zn(II) complexes. Carbonic anhydrase has been extensively reviewed in recent years,^{10–18} and work in our laboratories has focused on the study of functional models for carbonic

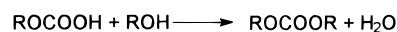
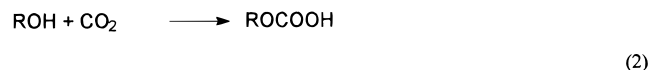
anhydrase.^{19–21} Model complexes^{20–22} are not only employed to mimic the active site of carbonic anhydrase, which is characterized by a p*K*_a value of ca. 7, but also to investigate the characteristic pH dependence of both the catalyzed hydration and dehydration reactions^{19,20} (see ref. 20 for a detailed account on model Zn(II) complexes). The best functional models reported up to now are the 1,5,9-triazacyclododecane ([12]-aneN₃) and 1,4,7,10-tetraazacyclododecane ([12]aneN₄, cyclen) complexes of Zn(II) in the form Zn(L)H₂O²⁺ and Zn(L)-OH⁺.^{19,20} The highest catalytic activity for the hydration of CO₂ has been reported for Zn(cyclen)OH⁺,²⁰ which is only one order of magnitude less reactive than HCA III²² but 4 orders of magnitude less than HCA I.²³ The general accepted mechanism for the hydration reaction consists of the steps outlined in (1), which can account for the characteristic pH dependence observed for this process.



If ROH instead of H₂O is employed as solvent, it should in principle be possible to perform the reactions outlined in (2): Solvolysis of CO₂ leads to the formation of a monoalkyl or monoaryl carbonate, which during a subsequent esterification leads to the dialkyl or diaryl carbonate. These reactions are in principle simple solvolysis and hydrolysis processes and involve

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no redox chemistry. To what extent can these reactions be catalyzed by the model Zn(II) complexes referred to above?

Along these lines, Kato and Ito^{24–26} have reported the first evidence that a series of tetraazacycloalkane complexes of Zn(II) can take up CO₂ in alcoholic medium to produce a series of monoalkyl carbonate complexes of the type [Zn(L)(O₂COR)]·ClO₄ (L = [14]aneN₄, Me₂[14]aneN₄, Me₄[14]aneN₄; R = Et, Me) and [Zn(L)]₃(O₂COR)₂(ClO₄)₄ (L = [15]aneN₄; R = *n*-Bu), of which three structures were confirmed by X-ray analysis.²⁵ The CO₂ uptake reaction was found to be facilitated by the addition of a base (B) such as NaOR or NEt₃, which suggests that the monoalkyl carbonate complex is formed in the direct reaction of Zn(L)²⁺ with ROCO₂[−], produced via reaction 3, and



not via CO₂ uptake by an alcohol complex. In later work²⁶ monomethyl carbonato complexes of Ni(II), Cu(II), and Co(II) with tetraazacycloalkane chelates were prepared via CO₂ uptake reactions.

Recently, Ruf and Vahrenkamp²⁷ found that (Tp^{Cum,Me}Zn–OH) complexes (Tp^{Cum,Me} = hydrotris(3-*p*-cumenyl-5-methylpyrazolyl)borate) react with species containing a cumulated double bond such as CO₂, CS₂, SO₂, or R–NCS. With CO₂ a monoalkyl carbonato complex (Tp^{Cum,Me}Zn–O–CO–OR, R = Me, Et)^{27a} is formed, and the X-ray structure for R = Me was reported. They also observed a decisive influence of the substituents of the Tp ligand on the nucleophilicity of TpZn–OH and therefore on the reactivity toward CO₂. Whereas (Tp^{Cum,Me}Zn–O–CO–OR) is formed readily from CO₂, (Tp^{tBu,Me}Zn–O–CO–OR)^{27b} is only formed by the reaction of (Tp^{tBu,Me}Zn–OH) (Tp^{tBu,Me} = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate) with dialkyl dicarbonate (MeOCOOCOMe), and (Tp^{tBu,tBu}Zn–OH) is unreactive toward both electrophiles. Although they could convert stoichiometric amounts of monoethyl carbonato complexes into diethyl carbonate, this reaction path is still far from a catalytically useful process.

Our efforts to convert CO₂ to organic carbonates based on the hydration mechanism of carbonic anhydrase and the general concept outlined in (1) and (2) were not successful, and a brief account of the work performed is presented here. In addition, we isolated {[Zn(cyclen)]₃(μ₃-CO₃)}(ClO₄)₄ and [Zn(cyclen)-EtOH](ClO₄)₂ from the alcoholic reaction mixtures and report their X-ray crystal structures. The results are discussed in terms of the suggested mechanism for the formation of carbonato complexes.

Experimental Section

Materials. All zinc salts were of reagent grade and used without further purification. 1,4,7,10-Tetraazacyclododecane (cyclen) was prepared according to the method of Richman and Atkins.²⁸ Methanol and ethanol were of analytical grade (99.8%) and not further dried unless otherwise indicated. Ba¹³CO₃ was purchased from Aldrich and used as received. [Zn(cyclen)(OH₂)](ClO₄)₂ was prepared according to literature methods.²⁰

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[Zn(cyclen)EtOH](ClO₄)₂. An ethanolic solution of Zn(ClO₄)₂·6H₂O was added dropwise to an ethanolic solution of cyclen under stirring at 50–60 °C. After 1 h the reaction mixture was cooled to room temperature and concentrated under reduced pressure to yield a white precipitate. This product was recrystallized from ethanol and allowed to stand in a refrigerator for several weeks. Colorless block crystals were obtained, suitable for X-ray analysis. Yield = 30%. Due to the extremely weak coordinated ethanol, the complex is only stable in ethanolic solution and, therefore, no elemental analysis of the isolated crystal could be performed.

{[Zn(cyclen)]₃(μ₃-CO₃)}(ClO₄)₄. A 1.24 g (3.32 mmol) amount of Zn(ClO₄)₂·6H₂O was dissolved in 10 mL of alcohol (ethanol or methanol) and added dropwise to a stirred solution of 572 mg (3.32 mmol) of cyclen at room temperature while bubbling CO₂ through the reaction mixture. The CO₂ flow was continued for several hours, and a white precipitate was obtained. This product was filtered off and recrystallized from alcohol–acetonitrile (1:1). The solution was allowed to stand at room temperature for several weeks. Colorless cubic crystals were obtained, suitable for X-ray analysis. Yield = 80%.

¹H-NMR: 2.75 ppm (s, CH₂); 3.85 ppm (s, NH). ¹³C-NMR: 167.5 ppm (CO₃, carbonate); 45.7 ppm (CH₂; ligand of the non-carbonate complex); 43.4 ppm (CH₂; ligand of the carbonate complex). Anal. Calcd for {[Zn(cyclen)]₃CO₃}(ClO₄)₄·4H₂O: C, 25.17; N, 14.99; H, 4.77. Found: C, 25.52; N, 14.11; H, 5.16.

{[Zn(cyclen)]₃(μ₃-¹³CO₃)}(ClO₄)₄. ¹³CO₂ was released from 2.0 g (10.1 mmol) of Ba¹³CO₃ by adding slowly 20 mL of diluted HCl and bubbled through a solution containing equimolar amounts of Zn(ClO₄)₂·6H₂O and cyclen. The solution was kept under ¹³CO₂ atmosphere for several hours to complete the CO₂ uptake reaction. A white precipitate was obtained, after recrystallization from alcohol–acetonitrile (1:1).

¹H-NMR: 2.75 ppm (CH₂); 3.85 ppm (NH). ¹³C-NMR: 167.7 ppm (CO₃; carbonate); 124.2 ppm (CO₂); 45.5 ppm (CH₂; ligand of the non-carbonate complex); 43.2 ppm (CH₂; ligand of the carbonate complex).

{[Zn(cyclen)]₃(μ₃-CO₃)}(ClO₄)₄ (Synthesis with LiCO₃Me). A 75 mg (0.92 mmol) amount of LiCO₃Me and 400 mg (0.92 mmol) of zinc cyclen complex in 10 mL of methanol were stirred over a period of 24 h. The resulting solid was filtered off and dried in air.

¹H-NMR: 2.75 ppm (s, CH₂); 3.85 ppm (s, NH). ¹³C-NMR: 167.4 ppm (CO₃, carbonate); 45.7 ppm (CH₂; ligand of the non-carbonate complex); 43.3 ppm (CH₂; ligand of the carbonate complex).

Instrumentation. Infrared spectra were recorded on Nicolet 5SX and Mattson Polaris spectrometers using the KBr pellet method. ¹H- and ¹³C-NMR measurements were performed on a Bruker DPX 300 (300 MHz) NMR spectrometer with DMSO-*d*₆ as solvent. Reactions in supercritical CO₂ were performed in a 250 mL V4A steel high-pressure laboratory autoclave Model II from Roth, equipped with a PTFE inset and attached to a PM-101 compressor from NWA, Lörrach, Germany.

X-ray Crystal Structure Analysis. {[Zn(cyclen)]₃(μ₃-CO₃)}(ClO₄)₄·2H₂O (**1**). Colorless blocks of **1** were grown at room temperature from a saturated solution in acetonitrile–ethanol (1:1). A colorless cubic crystal (0.4 × 0.3 × 0.2 mm³) was sealed in a glass capillary and mounted on a Philips PW1100/1 diffractometer. Unit cell parameters were determined from automatic centering of 22 reflections (17° < θ < 19°) and refined by least-squares methods. Intensity data were collected with graphite-monochromatized Mo Kα radiation, using the ω-scan technique. A total of 10 410 reflections were collected (−21 ≤ *h* ≤ 21, 0 ≤ *k* ≤ 21, 0 ≤ *l* ≤ 21), of which 2805 were unique with *F*_o > 4σ(*F*_o). Machine parameters, crystal data, and data collection parameters are summarized in Table 1. Selected bond distances and bond angles are given in Table 2.

{[Zn(cyclen)(EtOH)](ClO₄)₂·EtOH (2). Colorless blocks of **2** were grown at room temperature from a saturated solution in ethanol. A colorless crystal (0.7 × 0.6 × 0.4 mm³) was sealed in a glass capillary and mounted on an Enraf-Nonius MACH3 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections (17° < θ < 19°) and refined by least-squares methods. Intensity data were collected with graphite-monochromatized Mo Kα radiation, using the ω/2θ-scan technique. A total of 8778 reflections were collected (−15 ≤ *h* ≤ 15, 0 ≤ *k* ≤ 13, −18 ≤ *l* ≤ 18), of which 3011 were unique with *F*_o > 4σ(*F*_o). Machine parameters, crystal data, and data

Table 1. Crystallographic Data from the X-ray Diffraction Study of {[Zn(cyclen)]₃(μ₃-CO₃)(ClO₄)₄}·2H₂O (**1**) and {[Zn(cyclen)EtOH](ClO₄)₂}·EtOH (**2**)

	1	2
empirical formula	Zn ₃ Cl ₄ O ₁₉ N ₁₂ C ₂₅ H ₆₀ ·2H ₂ O	ZnCl ₂ O ₉ N ₄ C ₁₀ H ₂₆ ·EtOH
<i>a</i> , Å	21.850(5)	12.707(5)
<i>b</i> , Å	21.850(5)	11.780(5)
<i>c</i> , Å	21.850(5)	15.642(5)
α, deg	90	90
β, deg	90	105.250(5)
γ, deg	90	90
<i>V</i> , Å ³	10431.7(41)	2259.0(15)
<i>Z</i>	8	4
<i>fw</i>	1206.80	528.69
space group	<i>Pbca</i>	<i>P2₁/n</i>
ρ(calcd), g cm ⁻³	1.537	1.554
λ(Mo Kα), Å	0.710 69	0.710 69
μ, cm ⁻¹	1.646	1.362
<i>R</i> ₁ ^a	0.088	0.046
<i>R</i> _w ^b	0.2146	0.1488
<i>T</i> , K	293(2)	293(2)
<i>F</i> (000)	4736	936

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths			
Zinc Environment			
Zn(1)–O(1)	1.950(4)	Zn(2)–N(7)	2.167(5)
Zn(1)–N(1)	2.144(5)	Zn(2)–N(8)	2.143(5)
Zn(1)–N(2)	2.173(5)	Zn(3)–O(3)	1.960(4)
Zn(1)–N(3)	2.154(5)	Zn(3)–N(11)	2.116(5)
Zn(1)–N(4)	2.111(5)	Zn(3)–N(12)	2.132(5)
Zn(2)–O(2)	1.943(4)	Zn(3)–N(10)	2.144(5)
Zn(2)–N(5)	2.120(5)	Zn(3)–N(9)	2.173(5)
Zn(2)–N(6)	2.140(5)		
Carbonato Environment			
O(1)–C(25)	1.285(4)	O(3)–C(25)	1.294(4)
O(2)–C(25)	1.287(4)		
Bond Angles			
Zinc Environment			
O(1)–Zn(1)–N(4)	119.1(2)	N(6)–Zn(2)–N(8)	136.8(2)
O(1)–Zn(1)–N(1)	113.3(2)	N5–Zn(2)–N(7)	137.3(2)
N(4)–Zn(1)–N(1)	82.6(2)	N(6)–Zn(2)–N(7)	82.2(2)
O(1)–Zn(1)–N(3)	108.9(2)	N(8)–Zn(2)–N(7)	80.9(2)
N(4)–Zn(1)–N(3)	82.9(2)	O(3)–Zn(3)–N(11)	119.9(2)
N(1)–Zn(1)–N(3)	137.3(2)	O(3)–Zn(3)–N(12)	109.5(2)
O(1)–Zn(1)–N(2)	103.2(2)	N(11)–Zn(3)–N(12)	82.6(2)
N(4)–Zn(1)–N(2)	137.6(2)	O(3)–Zn(3)–N(10)	113.2(2)
N(1)–Zn(1)–N(2)	82.4(2)	N(11)–Zn(3)–N(10)	82.8(2)
N(3)–Zn(1)–N(2)	81.9(2)	O(2)–Zn(2)–N(7)	102.9(2)
O(2)–Zn(2)–N(5)	119.7(2)	N(12)–Zn(3)–N(10)	136.6(2)
O(2)–Zn(2)–N(6)	112.4(2)	O(3)–Zn(3)–N(9)	103.6(2)
N(5)–Zn(2)–N(6)	83.6(2)	N(11)–Zn(3)–N(9)	136.5(2)
O(2)–Zn(2)–N(8)	110.0(2)	N(12)–Zn(3)–N(9)	81.1(2)
N(5)–Zn(2)–N(8)	82.7(2)	N(10)–Zn(3)–N(9)	82.0(2)
Carbonato Environment			
C(25)–O(1)–Zn(1)	116.6(2)	O(1)–C(25)–O(2)	120.1(3)
C(25)–O(2)–Zn(2)	116.3(2)	O(1)–C(25)–O(3)	119.3(3)
C(25)–O(3)–Zn(3)	115.6(2)	O(2)–C(25)–O(3)	120.5(2)

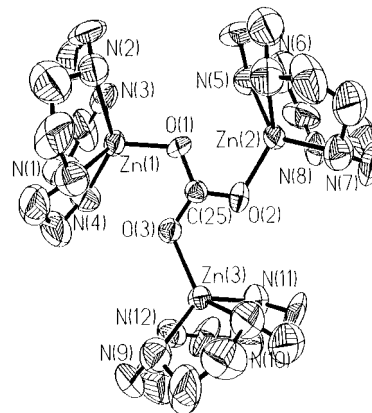
collection parameters are summarized in Table 1. Selected bond distances and bond angles are given in Table 3.

Results and Discussion

Description of the X-ray Structure of {[Zn(cyclen)]₃(μ₃-CO₃)(ClO₄)₄}·2H₂O (1**).** A labeled diagram of compound **1** is shown in Figure 1. The μ₃-bridged carbonato complex possesses a pseudo-3-fold molecular symmetry. Each of the three zinc ions is five-coordinated with the four nitrogen donor atoms in one plane and one oxygen of the carbonate ligand. The metal centers are shifted from the carbonate plane by 18.8 pm. The coordination environment of the zinc ions can be

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Zn–O(9)	1.982(3)	Zn–N(1)	2.151(5)
Zn–N(2)	2.108(4)	O(9)–C(9)	1.444(9)
Zn–N(3)	2.122(4)	C(9)–C(10)	1.471(10)
Zn–N(4)	2.130(5)		
O(9)–Zn–N(2)	118.5(2)	O(9)–Zn–N(1)	109.0(2)
N(2)–Zn–N(3)	82.7(2)	N(2)–Zn–N(1)	82.5(2)
O(9)–Zn–N(4)	103.4(2)	N(3)–Zn–N(1)	138.8(2)
N(2)–Zn–N(4)	138.1(2)	N(4)–Zn–N(1)	82.7(2)
N(3)–Zn–N(4)	83.2(2)	O(9)–C(9)–C(10)	115.6(7)

**Figure 1.** ORTEP view of **1**.

described as distorted square pyramidal. The four nitrogen atoms of the cyclen macrocycle ligand form a plane, and the zinc ion is shifted by 78.7 pm above this plane. The isolated and characterized μ₃-CO₃ complex of Zn(cyclen) exhibits structural properties similar to those for a series of such complexes summarized in Table 5. The Zn–O bond lengths in [(ZnL)₃(μ₃-CO₃)(ClO₄)₄] are typical for five-coordinate Zn(II) complexes, and in a couple of cases the Zn center is 30–90 pm above the chelate (N₄) plane.

¹³C-NMR Spectra. Due to the low solubility of complex **1** the signal for the μ₃-CO₃ carbon atom is very weak. Labeling this complex with ¹³CO₂ revealed a sharp singlet at 167.5 ppm for the μ₃-CO₃ group and a signal for free ¹³CO₂ at 124.4 ppm. The chemical shift for the μ₃-CO₃ carbon atom lies in between the values reported for unidentate carbonate complexes of the type Zn–O₂C–OR²⁴ and dinuclear μ₂-carbonato bridged species (Zn–OCO₂–Zn) of 169–172 ppm.²¹ Furthermore, the labeling allowed us to show that in DMSO an equilibrium between the bridged complex and Zn(cyclen) exists. In contrast to Kato and Ito,²⁴ who reported evidence for a Zn–OR species, no such signals were observed. From the crystal structure of **2**, however, we conclude that such a species must exist as a labile intermediate. The found equilibrium also accounts for the fact that only weak signals for the carbonate group in the NMR spectra were observed. It follows that such spectra must be recorded under saturated CO₂ conditions.

Description of the X-ray Structure of {[Zn(cyclen)EtOH](ClO₄)₂}·EtOH (2**).** Figure 2 shows a labeled diagram of compound **2**. The Zn atom is five-coordinate with the four nitrogen donor atoms and the oxygen of the coordinated ethanol. The coordination of the Zn atom can be described as distorted square pyramidal. The Zn–O bond distance of 198.2 pm lies in the typical range between 194 to 203 pm for similar five-coordinated Zn complexes²⁹ and is close to 199.4 pm, reported for Zn[N-(2-hydroxyethyl)cyclen], a complex containing an

(29) References 25, 30, 31, 33, and 34.

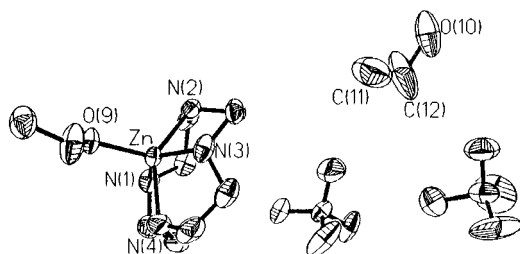
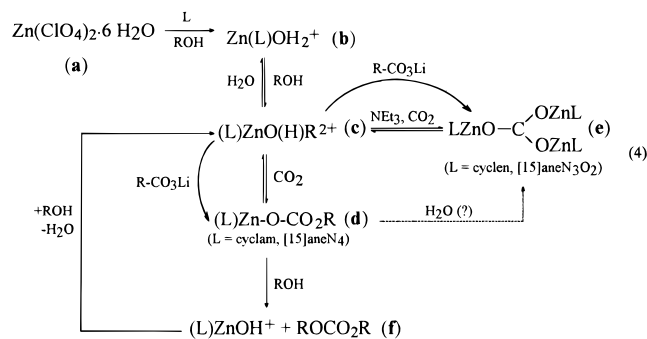


Figure 2. ORTEP view of **2**.

intramolecular Zn–O(H)Et bond.^{30a} In contrast to that, a deprotonated ethoxide complex, Zn[N-(2-hydroxyethyl)-1,5,9-triazacyclododecane],^{30b} exists as five-coordinate dimeric Zn(II) species with a Zn–O[−] bond length of 195.0 pm.

Mechanism of the Formation of Macrocyclic Zinc Carbonate Complexes. Carbonato complexes were synthesized by the addition of CO₂ to a metal–oxygen bond or by substituting a more labile ligand by the alkyl carbonate anion. In the first case, CO₂ is bubbled through alcoholic solutions of the macrocyclic complex containing a base (e.g. NEt₃) at room temperature. The complex can also be generated in situ by mixing alcoholic solutions of the ligand and the corresponding zinc salt at 50–60 °C. The subsequent addition of base followed by the bubbling of CO₂ through the reaction mixture results in the formation of carbonate complexes. The type of carbonate complex strongly depends on the ligand. Monoalkyl carbonate complexes are formed for [14]aneN₄, [15]aneN₄, Me₂[14]aneN₄, and Me₄[14]aneN₄24, whereas ligands such as [12]aneN₄ and [15]aneN₃O₂³¹ result^{32–35} in trimeric complexes of the type [LZn]₃(μ₃-CO₃) containing a triply bridging μ₃-CO₃ unit (see Tables 4 and 5). The reaction scheme in eq 4 is based on information obtained from the literature and our own observations.



The perchlorate salt of Zn(II) (**a**) was selected to avoid the coordination of other anions. Complexes of the type (L)-

ZnOH₂²⁺ (**b**) have been isolated and characterized.³⁶ This species activates alcohol via coordination to the metal center when coordinated H₂O is substituted. The isolation and characterization of [Zn([12]aneN₄)O(H)Et](ClO₄)₂ clearly indicates the initial formation of such solvento complexes in alcoholic medium (**c**). Also for cyclam ligands, Zn–OR species were identified by NMR.²⁴ For L = cyclam or [15]aneN₄, deprotonation of coordinated EtOH in the presence of NEt₃ enables the binding of CO₂ to produce an alkyl carbonato complex (**d**). As far as we know, macrocyclic monoalkyl carbonato complexes of Zn(II) have only been characterized for a series of cyclam and related chelates by Kato and Ito.^{24–26} A possible reason may be the larger ring size of the employed chelates.

The protonated species is expected to undergo a substitution reaction with ROCO₂[−], whereas the deprotonated complex is expected to take up CO₂ to produce (L)ZnOCO₂R⁺. ROCO₂[−] can also be produced directly from ROH and CO₂ in the presence of a base. When L = cyclen or [15]aneN₄, no monoalkyl carbonato species could be detected, but a μ₃-CO₃ (**2**, **e**) group is formed. The direct synthesis of a possible alkyl carbonato complex via a nucleophilic substitution reaction with LiCO₃Me in dry MeOH also resulted in the formation of the μ₃-CO₃ complex.

Yamamoto et al.³⁷ have synthesized monoalkyl carbonato complexes of Cu(I) via the reaction of CO₂ with ROCu(PPh₃)₂ (R = Et, C₆H₅CH₂) to produce ROCO₂Cu(PPh₃)₂. Darensbourg and co-workers³⁸ have been unsuccessful in determining the structures of these complexes since they found that the presence of adventitious H₂O impurities leads to the formation of the corresponding carbonates and bicarbonates, [(PPh₃)₂Cu]₂CO₃ and [(PPh₃)₂CuOCO₂H]₂, for which X-ray diffraction structures were reported. We therefore assume that also for L = cyclen a monoalkyl carbonato complex may exist as an unstable intermediate species that is hydrolyzed in the presence of traces of water to produce the isolated μ₃-CO₃ complex.

Attempted Synthesis of Dialkyl Carbonates from Alcohol and CO₂. On the basis of our earlier experience with CO₂ uptake and CO₂ hydration reactions to produce bicarbonate and carbonate,^{19,21} it was our objective to synthesize organic carbonates using Zn(L)O(H)R complexes as intermediates. In the final step in scheme (4) the reaction with ROH should lead to the formation of the dialkyl or diaryl carbonate (**f**) and recycle the catalytic species. The excess of water could be separated with aid of a drying agent or by working in supercritical CO₂.⁷

In the proposed reaction scheme the basicity of the coordinated ROH will determine the balance between the CO₂ uptake and ROCO₂[−] substitution reactions. A stronger Zn–OR bond will favor the CO₂ uptake reaction path. In the subsequent esterification the strength of the O–C bond in ZnOCO₂R is crucial. These bond strengths can to some extent be affected by the electron donor or acceptor properties of the chelate L. We therefore undertook a systematic series of studies of Zn(L) complexes in which the nature of L was gradually changed in order to affect the Zn–OR and O–C bond strengths as outlined above. In each case reactions with various ROH (alkyl, aryl), CO₂, and ROCO₂[−] (in the presence of a base) were tested.

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Table 4. ¹³C NMR Spectral Data (δ) for Zinc Carbonato Complexes in DMSO-*d*₆

complex	δ(¹³ C), ppm			
	carbonate	freeCO ₂	CH ₃	ligand
Zn([14]aneN ₄)(O ₂ COCH ₃)(ClO ₄) ^{25,26}	160.6	124.4	53.7	28.7, 48.4, 50.7, 24.9, 28.2, 46.9; 47.1, 49.7, 51.3
(Zn[12]aneN ₄) ₃ (μ ₃ -CO ₃)(ClO ₄) ₄	167.5			45.7, ^a 43.4 ^b
(Zn[12]aneN ₄) ₃ (μ ₃ - ¹³ CO ₃)(ClO ₄) ₄	167.5	124.4		45.5, ^a 43.2 ^b
(Tp ^{Cum,Me})ZnOCOR (R = Me, Et) ²⁷	158			

^a Signal for the ligand of the carbonate complex. ^b Signal for the ligand of the non-carbonate complex.

Table 5. IR and X-ray Data for Macrocyclic Complexes Containing a μ₃-CO₃ Unit

complex	L	ref	IR, cm ⁻¹				X-ray data			
							d(M-O), pm	d(O-C), pm	∠OCO, deg	d(M-CO ₃ plane), ^a pm
{[ZnL] ₃ (μ ₃ -CO ₃)}(ClO ₄) ₄	[12]aneN ₄	this work					195.9	129.4		16.9
							194.9	128.8		20.5
							194.3	128.8		19.0
{[ZnL] ₃ (μ ₃ -CO ₃)}(ClO ₄) ₄	[15]aneN ₃ O ₂	31					194.6			18.9 (av)
{[CuL] ₃ (μ ₃ -CO ₃)}(ClO ₄) ₄	[15]aneN ₃ O ₂	31					193.5			29.4 (av)
{[CuL] ₃ (μ ₃ -CO ₃)(ClO ₄) ₃ }(ClO ₄) ₃	Medpt	32a					196.3	130.6	119.5	18.9 (av)
{[NiL] ₃ (μ ₃ -CO ₃)(NCS) ₄ }	Medpt	32b	1520	1384	839	212.0	128.9	125.0	coplanar	
						217.9	130.7	117.1		
						214.2	127.0	117.9		
{[ZnL] ₃ (μ ₃ -CO ₃)}(ClO ₄) ₄ H ₂ O	N(CH ₂ py)	33	1610	1377	765	196.5	130.8		23	
						195.1	127.8		66	
						198.3	127.8		34	
{[ZnL] ₃ (μ ₃ -CO ₃)(H ₂ O) ₃ }(ClO ₄) ₄	(bpy) ₂	34	1476 vs	841 w	694 m	209	126	119		
					1423 s	209.7	127	125		
						197.6	131	116		
{[CuL] ₃ (μ ₃ -CO ₃)(H ₂ O) ₃ }(ClO ₄) ₄	pip	35	1460	840	752	195.6		129.4		
{[CuL] ₃ (μ ₃ -CO ₃)(H ₂ O) ₃ }(NO ₃) ₄	pip	35								

^a Distance of the three metal atoms from the CO₃ plane in pm. Average (av) or individual values are given as indicated.

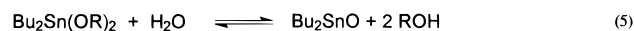
The main problem we encountered was the fact that tetra-*N*-substituted cyclen ligands (N-CH₂COOH, N-CH₂PO₃H, N-*n*-C₄H₉, N-COCCl₃) led to compounds that are insoluble in all common solvents. Although qualitative analysis (RFA) indicated that zinc complexes are formed and CO₂ is set free upon acidification, no unambiguous characterization by IR or NMR was possible.

The use of phenol or 2-ethylphenol instead of nonaromatic alcohols led to the same solubility problems so that the products could not be characterized. Furthermore, a number of ligands with different ring sizes and different C-substituents were tested. Zinc complexes with N₃-chelating ligands provide an additional free coordination site on the metal that could lead to an increase in reactivity for the final step (formation of dialkyl carbonates). [12]aneN₃ as well as 1,4-dioxocyclam and Tet A (=C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) did not result in products that could be properly characterized.

The reactions were also performed in supercritical CO₂. The reaction vessel contained ca. 200 mg of the zinc complex dispersed in approximately 60 mL of methanol and 50 mL of CO₂. The autoclave was kept at 90 bar and 50 °C for several hours. For the unsubstituted and -COCCl₃-substituted cyclen complexes, the same result was obtained as under 1 bar CO₂; i.e. a trimeric zinc complex containing a μ₃-CO₃ unit was formed and no further reaction occurred. The addition of molecular sieve to scavenge the produced water yielded no improvement. ([15]aneN₄)Zn-OCO-Me in ethanol under scCO₂ with added molecular sieve gave no reaction.

Kizlink and Pastucha³⁹⁻⁴¹ recently reported the formation of dimethyl carbonate from MeOH and CO₂ in the presence of

organotin and organotitanium complexes of the type Bu₂Sn(OR)₂ (R = Me, Et, Bu, Pr) and M(OR)₄ (R = Me, Et, Bu; M = Sn, Ti). Experiments³⁹ performed with dry ice as source for CO₂ resulted in partial decomposition of the organotin compounds by water according to reaction 5. In subsequent work,



gaseous CO₂ was employed and chemical scavengers of water, such as dicyclohexylcarbodiimide (DCC) and trimethyl phosphate, were employed in order to prevent the decomposition of the catalyst. High yields of (MeO)₂CO were obtained in the presence of DCC. These results clearly demonstrate the important role of moisture (H₂O) that can either decompose the catalyst or decompose the organic carbonate as discussed above. It is therefore expected that the unavoidable formation of H₂O in the reactions given in (2) will be an inherent difficulty to overcome.

We conclude from the findings in the present study that our adopted strategy to follow the mechanism for the catalyzed hydration of CO₂ in order to synthesize dialkyl and diaryl carbonates was not successful. A serious problem was encountered with traces of water, which is an inherent problem of the selected strategy and the low solubility of reactant and product complexes in alcoholic medium. We are convinced that a systematic tuning of the bond strengths in the Zn-O-R moiety could in principle induce the catalytic effect needed for the conversion of CO₂ to organic carbonates. Such a tuning will require a more drastic variation of the coordination sphere than performed in this study, by for instance the introduction of other donor ligands such as S and P.

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Acknowledgment. We gratefully acknowledge financial support for this work from Bayer AG. We kindly thank Dr. G. Liehr for the determination of the crystal structures.

Supporting Information Available: For the crystal structures of **1** and **2**, tables of complete crystal data, anisotropic thermal parameters,

equivalent isotropic displacement factors, full bond distances and angles, atomic coordinates, and mean plane calculations and ORTEP diagrams (24 pages). Ordering information is given on any current masthead page.

IC961368T