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Article

Formation of a Unique Zinc Carbamate by CO_2 Fixation: Implications for the Reactivity of Tetra-Azamacrocycle Ligated Zn(II) Complexes

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The macrocyclic ligand [13]aneN_4 (**L1**, 1,4,7,10-tetra-azacyclotridecane) was reacted with Zn(II) perchlorate and CO_2 in an alkaline methanol solution. It was found that, by means of subtle changes in reaction conditions, two types of complexes can be obtained: (a) the μ_3 carbonate complex **1**, $\{[Zn(\mathbf{L1})]_3(\mu_3\text{-}CO_3)\}(ClO_4)_4$, rhombohedral crystals, space group *R*3*c*, with pentacoordinate zinc in a trigonal bipyramidal enviroment, and (b) an unprecedenced dimeric Zn(II) carbamate structure, **2**, $[Zn(\mathbf{L2})]_2(ClO_4)_2$, monoclinic crystals, space group $P2_1/n$. The ligand **L2** (4-carboxyl-1,4,7,10-tetra-azacyclotridecane) is a carbamate derivative of **L1**, obtained by transformation of a hydrogen atom of one of the NH moieties into carbamate by means of CO_2 uptake. In compound **2**, the distorted tetrahedral Zn(II) coordinates to the carbamate moiety in a monodentate manner. Most notably, carbamate formation can occur upon reaction of CO_2 with the $[Zn\mathbf{L1}]^{2+}$ complex, which implicates that a Zn−N linkage is cleaved upon attack of CO_2. Since complexes of tetra-azamacrocycles and Zn(II) are routinely applied for enzyme model studies, this finding implies that the Zn-azamacrocycle moiety generally should no longer be considered to play always only an innocent role in reactions. Rather, its reactivity has to be taken into account in respective investigations. In the presence of water, **2** is transformed readily into carbonate **1**. Both compounds have been additionally characterized by solid-state NMR and infrared spectroscopy. A thorough comparison of **1** with related azamacrocycle ligated zinc(II) carbonates as well as a discussion of plausible reaction paths for the formation of **2** are given. Furthermore, the infrared absorptions of the carbamate moiety have been assigned by calculating the vibrational modes of the carbamate complex using DFT methods and the vibrational spectroscopy calculation program package SNF.

Introduction

The fixation of carbon dioxide by zinc hydroxide and alkoxide complexes has received considerable attention in the past. This interest is aroused from the fact that such reactions are closely related to the mode of action of the enzyme carbonic anhydrase, which catalyzes the reversible hydrolysis of CO_2 according to the equation $CO_2 + H_2O \rightleftarrows HCO_3^- + H^+$.[1,2] The active site of this enzyme consists of a zinc(II) center which is bound to three imidazole residues and a hydoxide ligand.

In order to gain a deeper understanding of the catalytic processes, zinc(II) hydroxide complexes of a variety of ligands have been prepared in the past two decades.[3] In particular, macrocyclic polyamines proved to be the ligands of choice to obtain highly functional model catalysts. The first example for such complexes, $[Zn([12]aneN_3)OH]^+$, has

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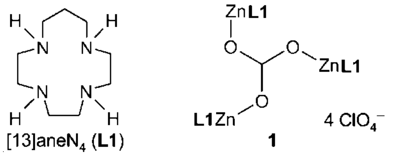
been reported by Kimura et al.[4,5] Van Eldik and Zhang described another example, $[Zn([12]aneN_4)OH]^+$, which is still the best synthetic catalyst for CO_2 hydrolysis in an aqueous medium.[6] These complexes are obtained very easily from aqueous solutions of the respective azamacrocyle and zinc(II) salts with noncoordinating anions, for example, perchlorate. Another approach has been worked out by Vahrenkamp and co-workers. Using the tris(pyrazolylborato) ligand system, they developed a series of structural models of the general formula $[Tp^{(R,R)}ZnOH]$.[7–10]

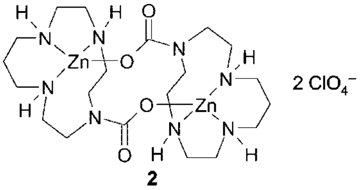
As CO_2 is a naturally overabundant and inexpensive C_1 building block, there have been attempts to make use of this catalytic activity to bind CO_2, namely, to obtain monoalkyl carbonates from alcohols in a catalytic reaction. In an alcoholic medium, however, no catalysis but rather simple CO_2 uptake reactions are observed. Investigations using zinc complexes of different tetra-azamacrocycles have been performed by Kato and Ito[11,12] and van Eldik et al.[13] These researchers found that monoalkylcarbonato complexes or μ_3-carbonato complexes are formed, depending on ring size and N substitution. More recently, Vahrenkamp and co-workers expanded their tris(pyrazolyl)boratozinc(II) approach to alkoxide complexes $[Tp^{(R,R)}ZnOR]$.[14–18] They reported that these compounds also react with CO_2 to yield monoalkylcarbonates, and an associated mechanism involving a four-center intermediate is discussed for this reaction.[14] Interestingly, the same concept is also applicable to sulfur-analogue systems: In a recent study, we examined the reactivity of some azamacrocyclic zinc thiolates $[LZn{-}SR]^+$ toward CS_2 and found a clean, reversible insertion reaction resulting in trithiocarbonate complexes $[LZn{-}S{-}C(S){-}SR]^+$.[19]

Along these lines, we investigated reactions of the azamacrocycle $[13]aneN_4$, zinc(II), base, and CO_2 in a methanolic solution. We obtained a carbonato complex similar to the one reported by van Eldik and Zhang but rather surprisingly also discovered the formation of a unique dimeric zinc carbamate (**2**) in which the azamacrocycle exhibits a coordination behavior hitherto unknown for this class of ligands. We thus performed a detailed analysis of the structural and spectroscopic properties of this complex. Moreover, there is apparently an increasing interest in metal carbamates which is rooted in the fact that such structures are featured in a number of enzymes, such as rubisco, urease, and phosphotriesterase. In the recent past, several articles have been published, covering synthesis[20,21] as well as computational studies on formation mechanisms[22,23] of zinc and lithium carbamates.[24] In this study, we discuss several aspects of carbonate and carbamate chemistry pertinent to zinc(II) complexes of azamacrocyclic ligands.

Scheme 1. Structures of Ligand $[13]aneN_4$ (**L1**) and Carbonate Complex $\{[Zn(\mathbf{L1})]3(\mu 3\text{-}CO_3)\}(ClO_4)_4$



Scheme 2. Structure of the Novel Carbamate Complex $[Zn(\mathbf{L2})_2(ClO_4)_2$ (**2**)



Results

Preparation of Zinc Complexes. In order to synthesize compound **1**, equimolar amounts of zinc perchlorate and $[13]aneN_4$ (**L1**) have been reacted for 15 min in methanol at room temperature, followed by the addition of 1 equiv of NaOH. After addition of CO_2 in the form of dry ice, a rapid precipitation of colorless cystals commences and the μ_3-carbonato complex **1** is obtained in high yield (Scheme 1).

When an attempt was made to obtain the methoxide complex $[Zn\mathbf{L1}(OMe)]ClO_4$, a solution was prepared as described above except for the addition of CO_2. It was kept at −30 °C in a sealed flask for some days. A minuscule amount of colorless crystals was found in the flask, and these were subjected to X-ray structural analysis and IR spectroscopy. The structural analysis revealed that formation of the dimeric carbamate **2** had occurred (Scheme 2), exhibiting a strong C=O stretching band at 1616 cm^{-1}. Since the preparation was not carried out under exclusion of ambient air, some CO_2 was apparently absorbed by the basic solution, thus leading to the observed result.

However, attempts to obtain a large portion of **2** in the described manner, that is, by the slow fixation of CO_2 from

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the air by alkaline solutions of [Zn**L1**] complexes, were not successful. Precipitates of **1** were obtained in all cases. Thus, we changed the synthetic procedure in order to deliberately generate carbamates: A solution of equimolar amounts of **L1** and NaOH in methanol was heated for several minutes. Then, CO_2 (dry ice) was added, and after a short standing time, 1 equiv of $Zn(ClO_4)_2{\cdot}6H_2O$ in methanol was slowly added. This procedure invariantly delivered mixtures of **1** and **2**, as was determined from the IR spectra. From elemental analyses, the content of carbamate was estimated to be 30−40% (varying results were obtained for different batches). The synthesis of a pure sample of **2** with an overall yield of 38% was finally achieved by the same procedure while excluding water to the best possible extent. This was done by using dry methanol and dry zinc perchlorate, which was obtained by heating the hexahydrate salt with an excess of triethyl orthoformate and subsequent drying in vacuo. The complex bis(carbamato) cation is stable in the solid state (a dry sample of compound **2** was found to be unchanged under ambient conditions after weeks) but slowly decomposes in solution (e.g., in DMSO). It is only poorly soluble in methanol; thus, traces of cocrystallyzing impurities can be removed by boiling in dry methanol and subsequent hot filtration. When treated with water, **2** is transformed readily into compound **1**. This is in good accordance with the observation that **2** is not formed in significant quantities in the presence of water due to the higher stability of **1**. We assume that decomposition occurs inversely to the formation of **2** (for the mechanism, see below).

Crystal Structure of 1. A diagram and structural parameters of the cation of **1** are given in Figure 1 and Table 1, respectively. Each zinc ion is coordinated to four nitrogens of the same macrocyclic ligand, and each of the three $[Zn\mathbf{L1}]^{2+}$ moieties is bound to one oxygen of the $\mu_3$bridging carbonate. Unlike van Eldik's related cyclen-based carbonate complex $\{[(Zn(cyclen))_3\ (\mu_3\text{-}CO_3)](ClO_4)_4\}{\cdot}2H_2O$,[13] the crystal exhibits a symmetry (space group $R3c$) and contains no solvent molecules. The cation possesses C_3 symmetry, the axis of the molecule being aligned perpendicular to the carbonate plane and passing through the carbonate carbon. The symmetry also includes one of the four perchlorate anions, the axis passing Cl and one oxygen atom. The zinc ions are almost perfectly located in the carbonate plane, the O−C−O−Zn dihedral of 177.9° being close to the ideal value of 180°. The three identical ZnL moieties exhibit Zn−N bond lengths in the range of 2.09−2.14 Å, which is in the usual range for zinc complexes of **L1**.[25] The Zn−O (1.956(3) Å) and carbonate C−O bond lengths (1.281(3) Å) are not significantly different from the average values in the cyclen analogon, showing average values of 1.952 and 1.288 Å, respectively.

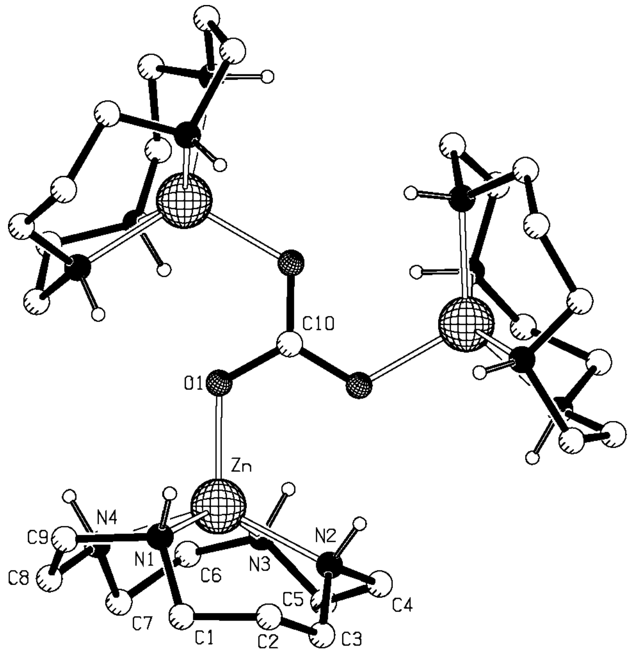

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Figure 1. Molecular structure of carbonate complex **1** (hydrogens on carbon atoms and perchlorate anions omitted).

Table 1. Selected Structural Data for Compound **1**

bond lengths [Å]		angles [deg]	
Zn−O	1.956(3)	Zn−O−C10	119.3(2)
Zn−N1	2.150(6)	N1−Zn−N2	90.1(3)
Zn−N2	2.090(6)	N2−Zn−N3	84.1(3)
Zn−N3	2.128(6)	N3−Zn−N4	84.6(3)
Zn−N4	2.141(5)	N4−Zn−N1	82.0(3)
O−C10	1.281(3)	N1−Zn−N3	153.5(2)
		N2−Zn−N4	137.6(3)

Crystal Structure of 2. The molecular structure of **2** (Figure 2 and Table 2) is the first example of a dimeric zinc(II) carbamate with 2-fold monodentate coordination, as is evident from the strong difference in Zn−O1 (2.83 Å) and Zn−O2 (1.92 Å) bond lengths. Moreover, just one comparable carbamato complex of zinc(II) with monodentate carbamate coordination has been described in the literature

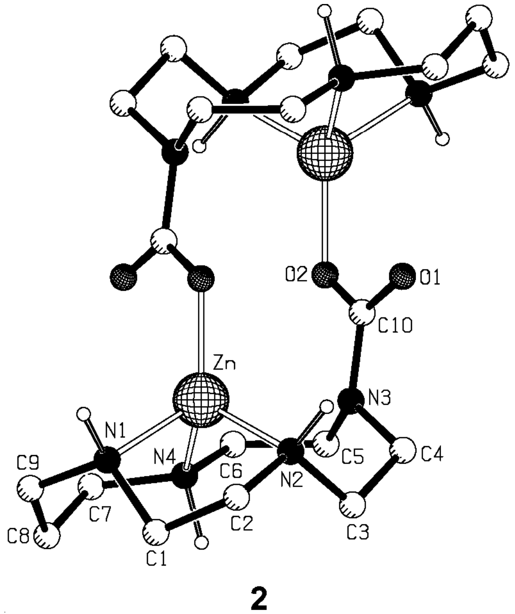

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Figure 2. Molecular structure of carbamate complex **2** (hydrogens on carbon atoms and perchlorate anions omitted).

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Table 2. Selected Structural Data for Compound **2**

bond lengths [Å]		angles [deg]	
Zn−O2	1.919(3)	Zn−O2−C10	112.0(3)
Zn−N1	2.083(5)	N1−Zn−N2	87.0(2)
Zn−N2	2.108(5)	N2−Zn−N4	112.0(2)
Zn−N4	2.026(5)	N4−Zn−N1	94.8(2)
C10−O1	1.230(6)	O2−Zn−N1	113.0(2)
C10−O2	1.287(6)	O2−Zn−N2	108.2(2)
C10−N3	1.404(6)	O2−Zn−N4	131.9(2)
		O2−C10−O1	125.0(4)
		O2−C10−N3	114.0(5)

until now.[26] The common coordination mode for carbamates at zinc centers is μ_2-bridging, for which several X-ray structures have been reported.[27–35]

Three of the four nitrogens are coordinated to the zinc(II) center. The carboxyl group of the carbamate is located at the fourth nitrogen, which is positioned between two ethylene bridges. The cation is centrosymmetric, which renders the structures of the two subunits identical (space group of the crystal is $P2_1/n$). The structural properties of the carbamate moiety and the N_3O ligated zinc center cannot directly be compared to the known literature example[26] in which the zinc shows N_4O coordination. Thus, the significant difference between the Zn−O bond distances (1.919(3) Å for **2**, when the literature value is 1.987(3) Å) comes at no surprise. The C═O (**2**, 1.230(6) Å; lit., 1.257(4) Å) and C−O bonds (**2**, 1.287(6) Å; lit., 1.297(5) Å) are identical within the error margins, but the carbamate's N−C bonds (**2**, 1.404(6) Å; lit., 1.348(6) Å) show a marked deviation, which we cannot explain plausibly.

Another point that deserves comment is the unusual configuration of the nitrogen atoms coordinating the zinc ion. These are chiral in nature, and the hydrogens can be positioned either toward the side of the carbamato ligand or, alternatively, toward the back side of the macrocycle. According to an established convention,[36,37] the hydrogen location of N substituents in azamacrocycles can be denoted with a (+) for "front" side and a (−) for "back" side positioning, respectively. For zinc complexes of **L1** as well as for 9- to 12-membered triazamacrocycles that bear one additional monodentate ligand, one normally observes an all-(+) configuration due to the small cavity of such ligands.[25,38] This applies, as expected, to compound **1**. For complex **2**, however, a (+ + −) configuration is adopted which has, to the best of our knowledge, no literature precedence. In addition, the tetrahedral coordination environment of the zinc ion is distorted to an unusual extent.

IR Spectra. A comparison of the fingerprint sections of IR spectra of compounds **1** and **2** is given in Figure 3. At first glance, the spectrum of **2** is much more complex, exhibiting additional strong absorptions. In order to assign these bands, we calculated the spectrum using the vibrational spectroscopy program package SNF (see Computational Details). According to this analysis, C−O valence is found at 1288 cm^{-1}, C−N valence at 1348 cm^{-1}, and C═O valence at 1616 and 1596 cm^{-1}. At 1454 and 1411 cm^{-1}, C−H deformation bands are observed, and a group of bending vibrations of the carbamate moiety is found around 800 cm^{-1}.

The $\nu_{C=O}$ absorption deserves additional comment. It is split into two separate bands owing to the fact that the vibrations of the two carbonyl groups are not independent. As indicated above, the molecule possesses C_i symmetry, rendering both carbamate units identical. However, the C═O vibration of the complete molecule possesses two different vibrational modes, one symmetric (A_g) and the other asymmetric (A_u), as depicted in Figure 3. The calculated values for those modes are $\nu_{C=O}(A_u) = 1627$ cm^{-1} and $\nu_{C=O}(A_g) = 1609$ cm^{-1}. This can be regarded as a very good match between experiment and theory, seconded only by the excellent accordance of the calculated and experimental differences of the two values (18 and 20 cm^{-1}, respectively). Furthermore, it is worth noticing that the calculation predicts the intensity of the symmetrical mode to be zero, which is rooted in the fact that computation is based on an isolated cation with ideal symmetry. The A_g mode exhibits no alteration of polarity and therefore is IR-inactive. In the crystal, however, this ideal behavior does not exist. Thus, the absorption is actually observed, although with a reduced intensity compared to the asymmetrical mode.

NMR Spectra. Acquisition of meaningful ^{13}C NMR spectra in solution is not possible for both complexes due to the poor solubility in most of the common solvents other than DMSO. Spectra in this solvent are of limited relevance: Compound **1** is apparently subject to dissociation, as no signal corresponding to the carbonate carbon could be detected. The carbamate **2** decomposed, and only the same spectrum as for compound **1** was obtained.

However, both the carbonate and carbamate carbon can be detected in solid-state NMR (for spectra, see the Supporting Information). The carbonate signal of **1** is a very narrow peak at 165 ppm, whereas the signal of the carbamate carbon of **2** is a much more broadened peak at 162 ppm. The methylene signals of both complexes are found in comparable ranges of the spectra. However, due to the similarity of these carbons, it is only possible to distinguish

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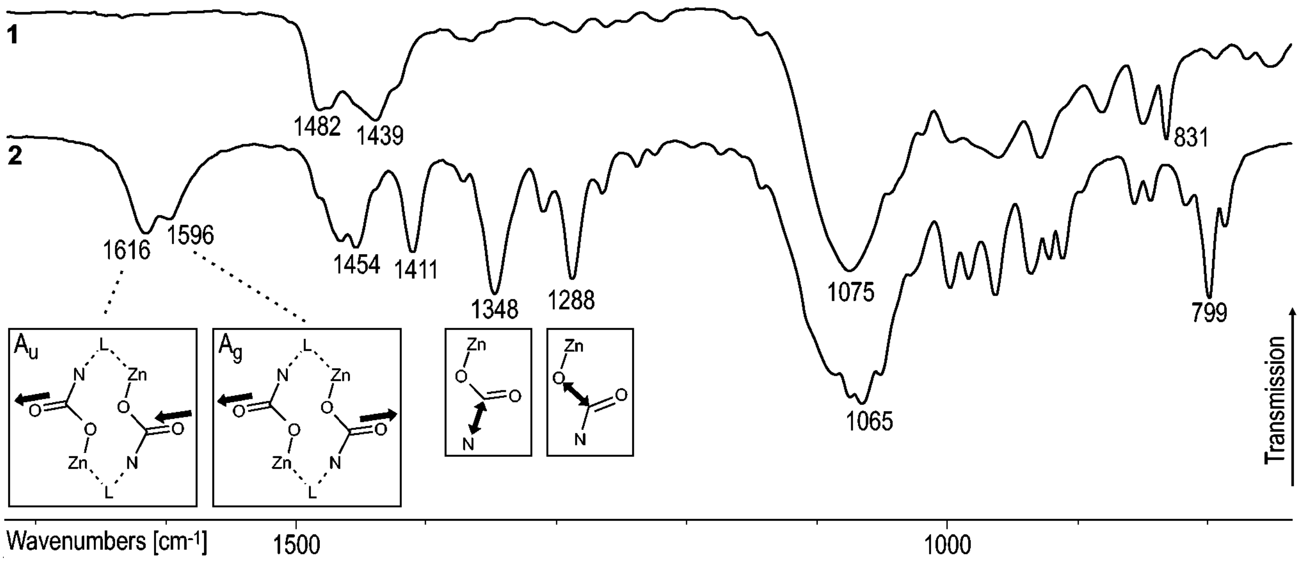
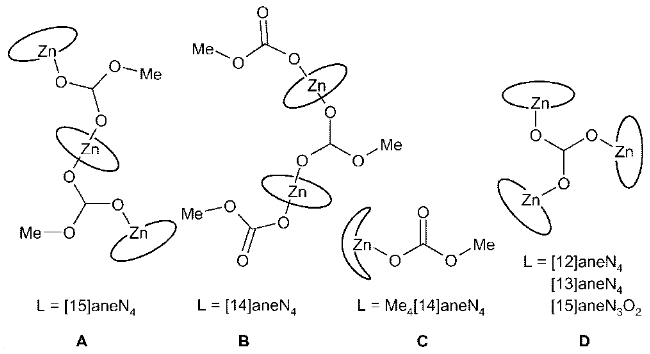


Figure 3. IR spectra (fingerprint sections) of complexes **1** and **2** and assignment of vibrational modes based on SNF calculation (see Computational Details).

Scheme 3. Known Solid-State Structures of Cationic Zinc(II) Carbonato Complexes with Different Tetra-Azamacrocycles, Obtained from Methanolic Solution (Additional Structural Information Taken from the Literature 12, 13, and 39). Azamacrocyclic Ligands **L** Are Indicated by Ellipsoid Shapes



between methylene carbons adjacent to nitrogens and the middle methylene group of the propylene bridge. The first are found as multiplets at 42−46 ppm for compound **1** and at 40−47 ppm for compound **2**, whereas the latter show shifts of 25 and 21 ppm for complexes **1** and **2**, respectively.

Discussion

Structural Diversity of Azamacrocycle Ligated Zinc Carbonates. The products obtained from reactions of azamacrocycle ligated zinc(II) with CO_2 in MeOH yield a variety of structures which are determined by size and N substitution of the macrocycle. Scheme 3 shows a summary of known structures of this type, which is based on studies of Kato and Ito (structure types A−C),[12] van Eldik et al. (type D with L = [12]aneN_4),[13] Bazzicalupi et al. (type D with L = [15]aneN_3O_2),[39] and this work (type D with L = [13]aneN_4). Structural representations (Ortep plots) are given in these papers. Kato and Ito first stated that the formation of monomethylcarbonates is reversible, the equilibrium being shifted toward the carbonato complex at low temperatures. Furthermore, they found that addition of amine bases, such as triethylamine or NaOR, markedly facilitates the reaction.

The mechanism of formation of all types of zinc carbonato complexes has been discussed in detail before.[11,13] Apparently, it is now generally agreed upon that in alcohols, carbonates are formed in the solution and are subsequently bound to the $[ZnL]^{2+}$ unit.[18] Although Vahrenkamp and coworkers also suggested a direct nucleophilic attack of zinc-bound alkoxide on CO_2 as an alternative pathway of monoalkylcarbonate formation,[14] they pointed out that such a mechanism is only valid for nonpolar solvents and the exclusion of water.[18]

Our aim was to elucidate the reason for the structural diversity observed for carbonato complexes of tetra-azamacrocycles. First of all, we like to draw attention to the fact that each azamacrocycle possesses a preferred configuration of the N-bound hydrogens when ligated to zinc(II), which we already discussed in earlier studies.[25,38] (An explanation of the notation of N-substituent positions is given above.) [15]aneN_4 can adopt (+ + + −) as well as (+ + − −) configuration, which enables $[Zn([15]aneN_4)]^{2+}$ moieties to function both as a terminal and a bridging unit in structure A. Both configurations have been found to coexist in solution.[25] In the case of terminal coordination, the (+ + + −) configuration is found, in which the alkyl bridges are heaped on one side of the $[ZnL]^{2+}$ unit. The bridging moiety features a (+ + − −) configuration, enabling coordination of methylcarbonate at two opposing axial positions.

The latter configuration is also adopted exclusively by the $[Zn([14]aneN_4)]^{2+}$ moiety in structure B, which exhibits a strong preference for this combination of N−H positions due to the symmetry of the ligand [14]aneN_4 (cyclam). To the best of our knowledge, there is no 3d metal complex of cyclam in which another configuration has been observed. In principle, a terminal coordination could also be possible; however, according to a preceding study, a fifth monodentate ligand attached to a $[Zn(cyclam)]^{2+}$ unit is bound much

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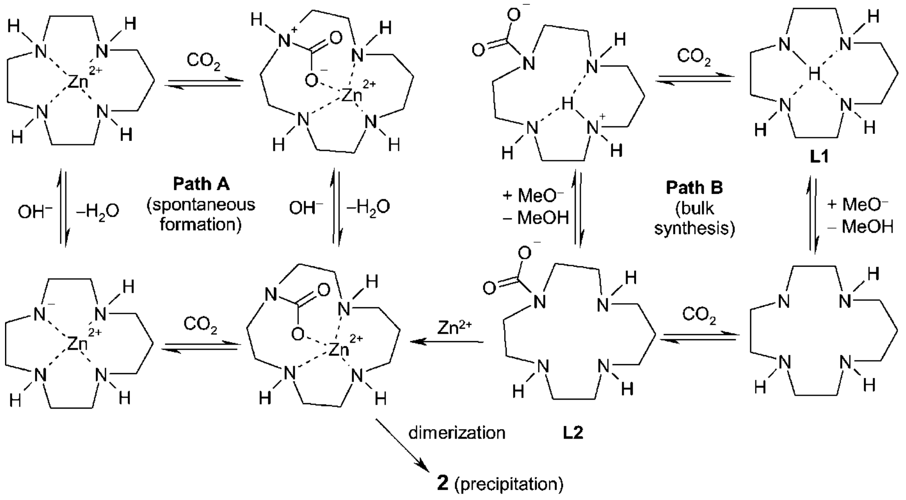
Scheme 4. Formation of the Novel Dimeric Carbamate **2**: Alternative Reaction Paths



weaker than in the case of other comparable ligands (namely, iso-cyclam, N-methyl-iso-cyclam, and [15]aneN_4).[25] As a consequence, this unit is found only in the bridging mode in its methyl carbonate complex. This is contrasted by Me_4[14]aneN_4 (tetramethylcyclam), which always adopts a (+ + + +) configuration in its metal complexes due to the kinetic impossibility of inversion of two of the R_2N-Me centers.[40] [Metal complexes of tetramethylcyclam featuring (+ + − −) configuration can only be obtained by N alkylation with the metal ion already being in place, that is, by methylation of the respective cyclam complexes].[37,41] In structure C, the macrocycle therefore does not possess a quasi-planar conformation comparable to the other rings but is almost completely surrounding the metal center, which is why only a terminal coordination is possible.

[12]aneN_4 (cyclen) and [13]aneN_4 are the only known tetra-azamacrocycles forming μ_3-carbonato complexes of type D under the given conditions and adopting (+ + + +) configuration in zinc(II) complexes. A causal relationship of these properties is obvious. We already pointed out that a small ring size in combination with this configuration causes an increased degree of exposition of the zinc ion, that is, a large displacement of the plane of the four ring nitrogens and therefore a reduced degree of sterical obstruction of the metal cation.[38] Thus, an arrangement of three $[ZnL]^{2+}$ units around a single carbonate is enabled, in contrast to the more sterically demanding moieties in structures A−C described above.

The complex based on [15]aneN_3O_2 cannot be directly compared to the other structures for two reasons: (i) Not all ring heteroatoms are involved in zinc ion binding. Basically, a N_3 coordination with an additional weak $Zn-OR_2$ interaction is found, which is why the compound is more comparable to complexes based on N_3 macrocycles. (ii) The ether linkages decrease the steric demand of the macrocycle and facilitate conformational change. The above considerations can therefore not be strictly applied to this ligand. Thus, despite its ring size and number of donor atoms, it does not obstruct the zinc ion to an extent comparable to the ligands L in structures A−C, and structure type D is also observed for this macrocycle.

With regard to these considerations, we hold the view that, in methanolic solution, formation of μ_3-carbonato complexes is generally preferred over methylcarbonato species. However, only $[ZnL]^{2+}$ units with a low degree of steric demand allow for formation of the first, which is why the latter are obtained in the presence of large ligands L.

Mechanism of Formation of the Carbamate Complex 2. The mechanism of carbamate formation in methanolic solution is of particular interest since, recently, a similar reaction has been reported: A large azamacrocycle with 28 ring atoms including a terpyridine moiety was found to form copper and zinc complexes capable of absorbing atmospheric CO_2, resulting in monomeric complexes with an intramolecular carbamate bridge.[20] Furthermore, Himmel investigated the formation of zinc(II) carbamates from the respective amides using quantum chemical calculations.[22] However, this study is of limited relevance for the present problem since the influence of the protic solvent has to be taken into account.

We would thus like to propose a possible mechanism for the formation of **2** under these conditions. In Scheme 4, hypothetical formation mechanisms for compound **2** are given. Two different reaction pathways of carbamate formation have to be considered, as complex **2** has been obtained under different conditions. Path A is suggested for the spontaneous formation of **2** from a basic methanolic solution of $[Zn\mathbf{L1}]^{2+}$ in presence of small amounts of CO_2, whereas path B is valid for the bulk synthesis of **2** (see also Experimental Section).

For path A, two possibilities can be discussed: The first is initial deprotonation of metal-coordinated nitrogen, leading to an amide structure capable of CO_2 binding. Although the presence of free amide is presumably limited to minuscule amounts due to reprotonation by the solvent, carbamate formation should nevertheless be possible in this way. The second is direct electrophilic attack of the CO_2 carbon

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on the zinc-bound nitrogen, promoted by the lewis-acidity of Zn^{2+}. This is also conceivable since the lewis acid Zn(II) can polarize the C=O linkage of CO_2, thus facilitating electrophilic attack on the ring nitrogen. However, a simultaneous deprotonation of this nitrogen would certainly be required for formation of the carbamate. In conclusion, we hold the view that a more or less concerted deprotonation of N−H and formation of the $N-CO_2$ bond occurs, which would equal a blend of the two possibilities given above.

For discussion of path B, one has to envision the proton-sponge properties of macrocyclic polyamines. These can lead to an increased basicity and even to superbasic systems. In the literature, X-ray structures for proton chelation of polyazamacrocyclic ligands were previously reported[42,43] that encourage the assumption of such structures for this reaction sequence. Yet, there are also two plausible scenarios: (i) Deprotonation of the ligand **L1**, leading to a free amide, which would doubtlessly be present only in very small quantities and, due to high nucleophilicity, quickly react with CO_2 to form the carbamate and (ii) direct reaction of **L1** with CO_2 and intermediate formation of a zwitterionic carbamate species, which we regard as the most probable mechanism. Such reaction would be analogous to the well-known spontaneous formation of carbamates from dialkylamines and CO_2. In this case, chelation of the ammonium proton would also have to be expected, thereby further stabilizing the intermediate. Zinc complexation and deprotonation should finally be a more or less concerted process.

The reactions of path B are clearly somehow equivalent to path A; we like to point out, though, that carbamate formation is apparently possible in the presence or absence of zinc ions, the latter being evidently more efficent. Further, to provide a rationale for the formation of the monomeric carbamate is certainly not sufficient to explain the observed formation of compound **2**. In the presence of water, fast decomposition of such a species is to be expected. However, as indicated above, dimer **2** is apparently hardly soluble in methanol as well as other solvents. We therefore believe that fast precipitation is the main driving force for the formation of complex **2**, causing even small amounts of carbamate to be quickly removed from the solution. The observed formation of **2** in the presence of water as described above is most likely due to the low temperature and the fact that only a minute amount of CO_2 was absorbed, thus promoting precipitation of **2** as well as preventing the simultaneous crystallization of the better soluble complex **1**. However, due to the delicate reaction conditions, it was found to be unfeasible to make this synthetic route useful for preparation.

Conclusions

In previous investigations, mechanistic aspects of reactions at tetra-azamacrocycle ligated zinc centers were discussed under the tacit assumption that, during their reactions, the Zn−N linkages remain unchanged. The persistence of this supposition to date is comprehensible, since as of yet no impetus has been given to challenge it. In fact, we are aware of just a single literature example giving reason to do so: In a recent study by Vargová et al. on ternary complexes of Zn(II), cyclen ([12]aneN_4), and pyridinecarboxylic acids, these authors also presented NMR-spectroscopic evidence for protonation of a $[Zn(cyclen)]^{2+}$ unit on one macrocycle nitrogen atom.[44] Their results suggest that, within a specific pH range, cyclen changes from four-dentate to three-dentate coordination. With respect to this work and our results, we hold the view that the hitherto assumed innocent role of the zinc azamacrocycle moiety has to be revised.

From the viewpoint of computational modeling of zinc enzymes, this idea appears not completely unfamiliar. As for computation, hypothetical complexes like $[Zn(NH_3)_3(OH)]^+$ and $[Zn(imidazole)_3(OH)]^+$ have been found to be very useful and valuable models for the His_3ZnOH structural motif of hydrolytic zinc enzymes, namely, carbonic anhydrase.[45–47] It may seem obvious to model $[N_4ZnOH]^+$ complexation environments, such as tetra-azamacrocycle ligated $[ZnOR]^+$ (R = H, alkyl, aryl) species, in a similar manner. However, such an approach is not straigth-forward; the location of zinc complexes with a N_4(O,S) coordination motif on the potential energy hypersurface is difficult at best for nonchelating ligands. On the other hand, no such problems exist if the coordinating atoms are part of a ring system, for example, azamacrocycles.[19] For the $[Zn(imidazole)_n(OH)]^+$ complexes, it has been shown by means of DFT calculation that the energy gained upon coordination of an additional imidazole decreases rapidly with increasing n up to $n = 3$.[48] However, by applying a similar computational approach, we could not locate a complex with $n = 4$. Upon structure optimization, one imidazole always inadvertently left the complex under formation of $[Zn(imidazole)_3(OH)]^+$. Coordination of the fifth ligand can therefore be considered to be rather weak, which is no surprise as N_4O ligated Zn(II) species are formally 20 VE complexes.

Thus, we conclude that the fourth nitrogen ligand of such compounds is generally apt to dissociation, which is also valid for chelators. The pentacoordinate Zn(II) in the tetra-azamacrocycle-based complexes of the above type is apparently only stable due to steric reasons, that is, the extraordinarily strong chelate effect of those ligands. In the case where one of the ring nitrogens is attacked by a proton or some small molecule, a change to four-coordinate zinc(II) is therefore possible and rather facile. Conversely, no such observations are to be expected for respective complexes of triazamacrocycles, as according to the above considerations, the three nitrogen ligands of the N_3O ligated Zn(II) can be regarded as being "just right" for zinc. Therefore, we hold

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the view that the future interpretation of reactions of tetra-azamacrocycle-based Zn(II) complexes necessarily should include a discussion on possible interactions of the substrates with the zinc-bound nitrogens. We deem this consideration being particularly obvious since no harsh or otherwise unusual reaction conditions were applied in the present case. Referring to the above statements, it should be worth the effort to set out for further systematic investigation of tri- and tetra-azamacrocyclic zinc(II) complexes to corroborate the proposed hypothesis.

Experimental Section

Materials and Methods. All reagents used were of analytical purity. Methanol was dried by dissolving a small amount of sodium and distillation under argon. The preparation of [13]aneN_4 followed essentially a published procedure,[49] with little alteration, as described earlier.[25] Standard NMR spectra were recorded using a Bruker AC 250 spectrometer. IR data were collected from the neat substances using a Nicolet Avatar 320 FT-IR spectrometer. Elemental analysis was performed using a Heraeus Vario EL III system. Melting points were determined with a Büchi Melting Point B 545 apparatus and are uncorrected. **Caution!** *Perchlorate salts are potentially explosive. Although we did not encounter any problems, the substances should always be handled with care and the necessary safety precautions followed.*

Synthesis of 1. [13]aneN_4 (**L1**; 1 mmol, 186 mg) was dissolved in methanol (50 mL). Then, a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 372 mg) in methanol (20 mL) was added and heated to 50 °C for 30 min. After the addition of NaOH (1 mmol, 10 mL of a 0.1 M solution in MeOH), CO_2 was added in the form of a small piece of dry ice, whereupon a colorless precipitate was formed instantly. (Alternatively, the solution may be left standing in an open flask, whereupon CO_2 from the air is slowly absorbed, leading to the same result.) Crystallization was completed by standing at room temperature for a few hours. The precipitate was filtered off and dried in vacuo. Yield: 277 mg (68%). m.p.: none. Decomposition above 340 °C. Anal. calcd for $C_{28}H_{66}N_{12}O_{19}Cl_4Zn_3$: C, 27.73; H, 5.49; N, 13.86; Cl, 11.69. Found: C, 27.63; H, 5.41; N, 13.81; Cl, 11.90. IR: 3316 w, 3298 m, 2945 m, 2886 m, 1482 s, 1439 s, 1075 vs, 960 s, 928 s, 831 s, 621 vs cm^{-1}. NMR ^{13}C (62.9 MHz, DMSO): 27.8, 44.0, 45.9, 48.4, 50.0 ppm. Solid-state NMR (^{13}C CP/MAS, 75.38 MHz): 25, 42, 46, 165 ppm.

Synthesis of 2. This synthesis was carried out under argon using the Schlenk technique. $Zn(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 1870 mg) was dissolved in triethylorthoformate (5 mL) and heated to 70−80 °C for 2 h. Then, all volatiles were removed and the colorless residue dried in vacuo. Dry MeOH (10 mL) was added, whereupon a clear solution was obtained.

NaOMe (25 mL of a 0.2 M solution in dry MeOH) was added to [13]aneN_4 (**L1**; 5 mmol, 930 mg) and stirred at 50 °C for 10 min. Then, dry ice (ca. 1 g) was added, and the solution was left standing for an additional 10 min. This mixture was transferred into a syringe and added to the warm (50 °C) solution of zinc perchlorate. After 30 s, a fine, colorless precipitate was formed. The crystallization process ceased after 10 min, whereupon the precipitate was filtered off, washed with a small amount of methanol, and dried in vacuo. Since the IR spectrum still indicated the presence of a small fraction of **1**, the material was suspended again in MeOH (100 mL), refluxed for 2 h, filtered off, washed with MeOH, and dried. Obtained was 750 mg (38%) of **2** as a fine, white powder. m.p.: none. Decomposition above 320 °C. Anal. calcd for $C_{20}H_{42}N_8O_{12}Cl_2Zn_2$: C, 30.47; H, 5.37; N, 14.22; Cl, 9.00. Found: C, 30.31; H, 5.24; N, 14.07; Cl, 9.27. IR: 3308 w, 3263 m, 3252 m, 2936 w, 2878 w, 1616 s, 1596 s, 1465 s, 1454 s, 1411 s, 1348 s, 1288 s, 1065 vs, 998 s, 963 s, 935 s, 799 s, 620 vs cm^{-1}. Solid-state NMR (^{13}C CP/MAS, 75.38 MHz): 21, 40, 47, 162 ppm.

Hydrolytic degradation of **2**: To a sample of **2** was added water, and the slurry was stirred overnight. In the mixture, a white solid was still present, which was filtered off, carefully dried, and subjected to IR spectroscopy. Spectra were identical to those of pure **1**.

Crystal Structure Determination. The intensity data were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo K(α) radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[50–52] The structures were solved by direct methods (SHELXS[53]) and refined by full-matrix least-squares techniques against Fo^2 (SHELXL-97[54]). The hydrogen atoms of the amine groups were located by difference Fourier synthesis. The coordinates were refined, and the thermal parameters were fixed. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered, nonhydrogen atoms were refined anisotropically.[54] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. The drawings in the paper were generated using PLATON.[55]

Crystal Data for 1.[56] $[C_{28}H_{66}N_{12}O_3Zn_3]^{4+} \cdot 4[ClO_4]^-$; $M_r = 1212.84$ g mol^{-1}; colorless prism; size = 0.05 × 0.05 × 0.05 mm^3; rhombohedral; space group $R3c$; $a = 22.1786(6)$; $b = 22.1786(6)$; $c = 16.4491(4)$ Å; $V = 7007.1(3)$ Å^3; $T = -90$ °C; $Z = 6$; $\rho_{calcd} = 1.724$ g cm^{-3}; (Mo Kα) = 18.42 cm^{-1}; F(000) = 3768; 14 957 reflections in h (−27/28), k (−28/26), l (−21/17); measured in the range $1.84° \le \Theta \le 27.50°$; completeness Θ_{max} = 99.9%; 3410 independent reflections; $R_{int} = 0.0455$; 3017 reflections with $F_o > 4\sigma(F_o)$; 199 parameters; 1 restraint; $R1_{obs} = 0.0500$; $wR_{obs}^2 = 0.1265$; $R1_{all} = 0.0606$; $wR_{all}^2 = 0.1346$; GOF = 1.029; Flack parameter 0.03(2); largest difference peak and hole = 0.758/−0.658 e Å^{-3}.

Crystal Data for 2.[56] $[C_{20}H_{42}N_8O_4Zn_2]^{2+} \cdot 2[ClO_4]^-$; $M_r = 788.26$ g mol^{-1}; colorless prism; size = 0.02 × 0.02 × 0.01 mm^3; monoclinic; space group $P2_1/n$; $a = 7.7588(2)$; $b = 14.6318(7)$; $c = 13.6349(7)$ Å; $\beta = 105.553(3)°$; $V = 1491.22(11)$ Å^3; $T = -90$ °C; $Z = 2$; $\rho_{calcd} = 1.756$ g cm^{-3}; (Mo Kα) = 18.61 cm^{-1}; F(000) = 816; 10 322 reflections in h (−9/10), k (−18/18), l (−17/14); measured in the range $2.78° \le \Theta \le 27.48°$; completeness Θ_{max} = 99.6%; 3401 independent reflections; $R_{int} = 0.0307$; 2686 reflections with $F_o > 4\sigma(F_o)$; 212 parameters; 0 restraints; $R1_{obs} = 0.0668$; $wR_{obs}^2 = 0.1827$; $R1_{all} = 0.0841$; $wR_{all}^2 = 0.1962$; GOF = 1.057; largest difference peak and hole: 1.695/−0.915 e Å^{-3}.

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Solid-State NMR. ^{13}C NMR spectra were acquired at 75.38 MHz (7 T) on a Bruker AMX-400 spectrometer using a 7 mm Bruker double-resonance probe at a spinning frequency of 5 kHz. A VACP/MAS pulse sequence with a 5 s, 90°, 1H pulse length and a ramped contact pulse of 5 ms on the x-channel was employed. During data acquisition, protons were decoupled by employing a tppm15 sequence with a 10 s pulse length, and 4096 scans were accumulated for each FID. The repetition time was set to 3 s. An exponential apodization with 24 Hz linebroadening was applied for data processing. Isotropic chemical shifts are referenced to TMS.

Computational Details. All calculations employ the density functional programs provided by the Turbomole 5.1 suite.[57] Results were obtained from Kohn–Sham optimizations of the investigated structure. We used the Becke-Perdew functional dubbed BP86[58,59] as implemented in Turbomole. Since the complex under investigation has a closed-shell electronic structure, we employed a restricted framework for the Kohn–Sham calculations. We applied the resolution-of-the-identity density-fitting technique with auxiliary basis sets by Eichkorn et al.[60,61] to speed up the calculations. For all atoms, we employed Ahlrichs' TZVP basis set featuring a valence triple-ζ basis with polarization functions.[62]

The molecular geometry obtained from the X-ray structural analysis served as starting point for the structure optimization. The perchlorate anion was omitted since its influence can be deemed to be negligible. In the crystal, the molecule possesses C_i symmetry. Therefore, all calculations were performed exploiting this molecular symmetry. The structure of the complex under investigation was fully optimized with a value of 10^{-4} as the convergence criterion for the norm of the Cartesian gradient; wave function convergence was set to better than 10^{-8} au in terms of the electronic energy change. The deviations between the calculated and the X-ray structure are small (bond lengths generally do not differ by more than 2−3 pm).

For the seminumerical calculation of vibrational frequencies and normal modes, the vibrational spectroscopy program package SNF[63] was used, which features a highly efficient massive parallelization as well as excellent restart facilities. Vibrational analysis using these theoretical methods has been recently reviewed.[64,65] All frequencies were used without scaling since previous investigations[66–68] demonstrated the reliability and accuracy of the BP86/TZVP method and yielded a scaling factor very close to unity.[69]

Individual vibrations were visualized using the program Molden.[70] The assignment of calculated vibrational modes to experimental bands as depicted in Figure 3 was done by regarding the vibrations in the respective ranges of the spectra.

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Supporting Information Available: X-ray crystallographic data in CIF format and ^{13}C SS-NMR spectra for compounds **1** and **2**, results of the frequency calculation (original SNF output, pseudo-Gaussian 98 format being readable, for example, by the program Molden[70]), and a xyz file with Cartesian coordinates of the calculated geometry of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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