Salicylaldimine Dizinc Complexes: Activation of Water Molecules and Fixation of CO_2 in the Coordination Sphere of Zinc

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Dedicated to Prof. Ernst Anders on the occasion of his 60th birthday

Keywords: Zinc / N ligands / N,O ligands / Carbon dioxide fixation / Enzyme models

Bi- and tetranuclear zinc complexes of the tridentate N,N,O ligand [{[2-(2-pyridyl)ethyl]imino}methyl]phenol (HL) and their enzyme-like reactions are described. The coordinated water molecules in a dizinc complex of this ligand can be deprotonated reversibly similar to those in the resting states of zinc enzymes. The resulting tetranuclear complex bearing bridging hydroxide ions allows the reversible uptake of CO_2. Whereas the coordination of hydrogen carbonate has not been observed, a tetranuclear carbonate complex with a unique structure was isolated. Its carbonate ion is coordinated to all four zinc atoms. The X-ray structures of the reported complexes are discussed.

Introduction

Zinc-containing enzymes accelerate the reversible hydration of carbon dioxide, the cleavage of peptide bonds, the hydrolysis of phosphate monoesters, and many other hydrolytic processes in biological systems with a high efficiency. The catalytic function of the zinc enzymes is not only essential for organisms but also of great theoretical interest. The activation of carbon dioxide and cleavage of amide and ester bonds in the coordination sphere of a metal also represent important reactions in synthetic chemistry. It is not surprising, therefore, that many efforts have been made to synthesize zinc-containing complexes that mimic the structural and functional features of the active centres in zinc enzymes.

Recent investigations revealed a distorted tetrahedral ligand geometry around the zinc ions in many zinc enzymes. Three coordination sites at their metal centres are coordinated by various amino acid residues (imidazolyl, -COOH, -SH), depending on the specific functions of the enzymes.[1] In the resting states of the enzymes, the fourth coordination site is occupied by a water molecule, which can be easily deprotonated, thus providing the catalytically active hydroxide form of the enzyme.

To synthesize zinc complexes by mimicking the active centres of mononuclear zinc enzymes, encapsulating tripodal hydrotris(pyrazolyl)borates (Tp ligands) and cyclen ligands are most frequently used. Vahrenkamp et al.[2−4] have developed the "Freiburg enzyme model" — zinc complexes with the aforementioned Tp ligands bearing sterically demanding substituents. Such complexes possess structural parameters similar to those of the active centre of the hydroxide and the water form of the zinc enzyme carbonic anhydrase (CA). The tetrahedral geometries around the zinc ions in these compounds are enforced by the pocket-like rigid Tp ligands. Parkin et al.[5] converted such a tetrahedral TpZnOH complex into the corresponding aqueous form by protonation and were even able to reverse this process. Tetrahedral zinc complexes with tripodal cyclen ligands like 1,5,9-triazacyclododecane have been reported to be some of the best functional models for CA.[6−10] Apart from the above examples, other more flexible unsymmetrical ligands with mixed N_xO_y donor environments have been established.[11−14] These ligands have been made to reproduce structural and functional properties of biologically relevant enzymes with more than one zinc ion in their active sites.

Zinc complexes with enzyme-analogous hydrolytic activities could be valuable in synthetic chemistry, too. However, the application of zinc complexes as catalysts for hydrolytic processes requires a deeper insight into their structure-reactivity relationship, and, especially, additional information about the reactivity of water molecules in the coordination sphere of zinc. In the present article, we describe bi- and tetranuclear zinc complexes of the Schiff base 2-[{[2-(2-pyridyl)ethyl]imino}methyl]phenol HL.

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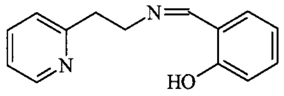

HL

Although the tridentate ligand chosen is not sufficiently rigid to enforce a tetrahedral geometry around the zinc centre, a zinc complex with coordinated and reactive water molecules is readily accessible. The Zn-OH_2 unit in this binuclear complex can be deprotonated by the addition of sodium hydroxide. Even the uptake of carbon dioxide is performed as a reversible pH-dependent process. However, attempts to isolate a complex with coordinated hydrogen carbonate were not successful. Only a carbonate-containing complex with an unusual structural motif was obtained. The above reactions were found to be very sensitive, and other products could be obtained under slightly different conditions. The complexes were characterized by X-ray structural determinations.

Results and Discussion

The binuclear complex **1** is formed by the reaction of equivalent amounts of HL, zinc perchlorate and sodium hydroxide in aqueous methanol. Compound **1** bears the deprotonated ligand L and a water molecule at both zinc ions. With less water in the solvent, the complexation yields the binuclear complex **2** with zinc-coordinated methanol molecules instead of the complexed water.

$[\mathbf{L}\ Zn(H_2O)]_2\,(ClO_4)_2$ $[\mathbf{L}\ Zn(CH_3OH]_2\,(ClO_4)_2$

1 **2**

Both complexes were subjected to X-ray structural determinations. The X-ray structural analysis of **1** and **2** revealed distorted square-pyramidal environments around the metal centres, which are linked by phenolate bridges (see Figure 1 and 2).

The coordinated water molecules in **1** are arranged in a *cis* configuration, whereas the methanol molecules in **2** are in a *trans* configuration. Both configurations are possible in dizinc complexes of L because of the flexibility of the ligand and the flexibility of the phenolate links. The water molecules in the coordination sphere of **1** are acidified in a similar manner to those in the Zn-OH_2 units of zinc enzymes. Therefore, this complex is accessible to a number of conversions.

In a methanolic solution of **1** with half an equivalent of sodium hydroxide at moderate temperatures (20−50 °C) under anaerobic conditions, one water molecule in **1** is deprotonated and the tetranuclear complex **3** is formed by dimerization.

$[(\mathbf{L}\ Zn)_2OH]_2\,(ClO_4)_2$

3

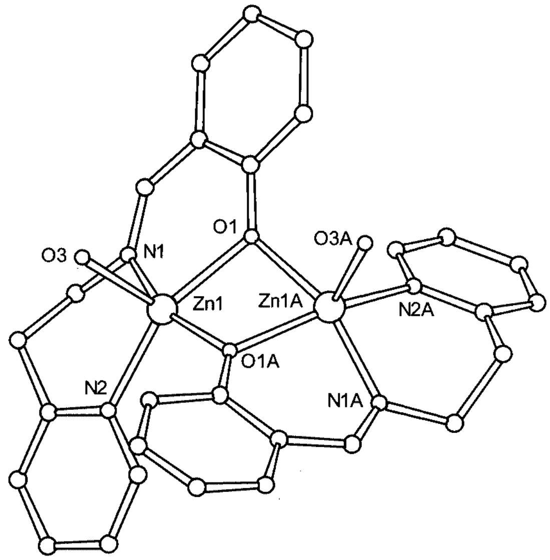

Figure 1. Molecular structure of **1** (cation only) with selected bond lengths [Å] and angles [°]: Zn1−O1 2.056(2), Zn1−O2 2.040(2), Zn1−N2 2.052(3), Zn1−N1 2.106(3), Zn1−O3 2.090(3), Zn2−O1 2.031(2), Zn2−O2 2.053(2), Zn2−O4 2.084(3), Zn1−Zn2 3.1035(6); O1−Zn1−N1 155.48(10), O1−Zn1−O3 102.62(10), O1−Zn2−O2 75.78(10), O1−Zn2−N4 160.93(10), O1−Zn2−O4 99.14(11), O1−Zn2−N3 98.15(10), O2−Zn1−O1 75.55(10), O2−Zn1−O3 98.55(12), O2−Zn1−N1 97.05(10), O2−Zn1−N2 160.43(11), O2−Zn2−N3 154.93(10), O2−Zn2−N4 87.09(11), O3−Zn1−N1 101.59(11), O4−Zn2−N3 102.11(11), N2−Zn1−O1 87.60(11), N2−Zn1−O3 94.73(13), N2−Zn1−N1 94.27(11), N4−Zn2−N3 93.86(11), N4−Zn2−O4 92.72(12), Zn1−O2−Zn2 98.62(10), Zn1−O1−Zn2 98.81(10)

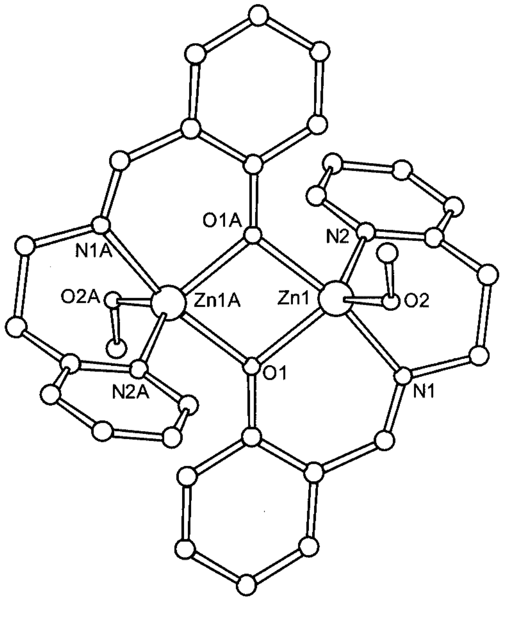

Figure 2. Molecular structure of **2** (cation only) with selected bond lengths [Å] and angles [°]: Zn1−O1 2.0154(10), Zn1−O2 2.0564(12), Zn1−O1A 2.0618(10), Zn1−N1 2.0697(12), Zn1−N2 2.0641(13), Zn1−Zn1A 3.1511(4); O1−Zn1−O2 114.96(5), O1−Zn1−O1A 78.78(4), O2−Zn1−O1A 95.63(5), O1−Zn1−N2 122.08(5), O2−Zn1−N2 122.92(5), O1A−Zn1−N2 96.88(5), O1−Zn1−N1 89.93(5), O2−Zn1−N1 89.62(5), O1A−Zn1−N1 168.70(5), N2−Zn1−N1 88.59(5)

Compound **3** has a dimeric structure with two identical binuclear halves linked via two Zn−OH−Zn bridges between the zinc ions. In **3**, all zinc ions are in distorted square-pyramidal coordination spheres and the metal centres in the halves are linked by phenolates as in complex **1**. The bond lengths and angles in the dizinc units of **3** are very similar to those in **1**. Therefore, **3** can be considered an OH-bridged dimer of **1**. Zinc complexes containing Zn−OH−Zn bridging moieties have been reported previously.[14−18]. The nonbonding distances between the zinc ions in the Zn−O−Zn moieties of **3** are 3.5 Å. Very similar Zn−Zn separations (3.55 Å, 3.61 Å) have been reported for other zinc complexes with only one hydroxide bridge between the zinc centres.[15,18] Compound **3** can be reprotonated to the water complex **1**. In the presence of a larger amount of sodium hydroxide the conversion of **1** becomes irreversible. Under these conditions, a ligand distribution reaction occurs. Zinc hydroxide is precipitated from the mixture and complex **4** is formed.

$[L_2\,Zn]_2\,[Na\,(MeOH)\,ClO_4]$

4

Its molecular structure is shown in Figure 3. Compound **4** can be considered as a dimer with two mononuclear complexes. The mononuclear halves of **4** are only linked by a fivefold coordinated sodium ion. In contrast to the other complexes reported here, two molecules of the deprotonated ligand are bound to each metal in **4**. The zinc ions in **4** are also fivefold coordinated and appear in a strongly distorted square-pyramidal geometry.

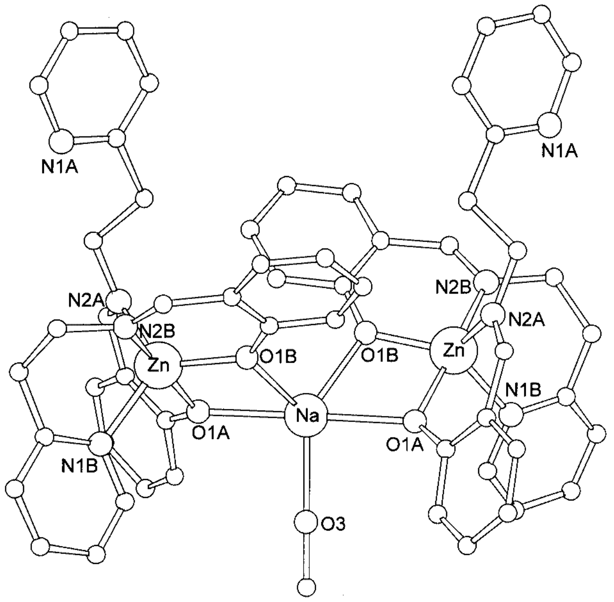

Figure 3. Molecular structure of **4** (cation only) with selected bond lengths [Å] and angles [°]: Zn−O1A 2.035(4), Zn−O1B 1.986(3), Zn−N1B 2.125(5), Zn−N2A 2.094(5), Zn−N2B 2.144(5), Na−O3 2.297(11), Na−O1A 2.385(3), Na−O1B 2.392(4); O1A−Zn−O1B 84.4(1), O1A−Zn−N1B 91.7(2), O1A−Zn−N2A 89.1(2), O1A−Zn−N2B 170.6(2), O1B−Zn−N1B 121.6(2), O1B−Zn−N2B 89.7(2), O1B−Zn−N2A 122.7(2), N2A−Zn−N1B 115.5(2), N1B−Zn−N2B 85.2(2)

The reactivity of **1** towards air and carbon dioxide has also been investigated. Carbon dioxide is taken up by deprotonated **1** in the presence of air. The gas is released again after the mixture has been acidified carefully. Similar to the hydration of CO_2 in the catalytic cycle of CA, this reaction is found to be reversible at moderate temperatures and is pH-dependent. The CA mechanism involves the formation of an intermediate with a Zn-CO_2H unit. It turned out to be impossible to isolate a complex with coordinated hydrogen carbonate. In the reaction of **1** with CO_2 from air and half an equivalent of NaOH, only the complex **3a** is obtained at moderate temperatures.

$[(L\,Zn)]_2\,(OH)]_2\,(ClO_4)_{2-x}\,(CO_3H)_x \qquad (0 < x < 1)$

3a

Its X-ray structure is presented in Figure 4. Compound **3a** contains the same coordination sphere as described for **3**. Only one perchlorate anion is partially replaced by hydrogen carbonate. The content of HCO_3^- in **3a** depends on the partial pressure of CO_2 in the atmosphere. The hydrogen carbonate is not formed by a simple absorption of carbon dioxide in an alkaline solution, because the reaction mixture does not contain any excess of hydroxide ions. The uptake of carbon dioxide can be explained by an intermediate interaction of CO_2 with the zinc centres in **3**.

At higher temperatures and in the presence of pure carbon dioxide, the CO_2 is incorporated into the coordination sphere of zinc, and the reaction provides the carbonate complex **5**.

$[(L\,Zn)_4\,CO_3\,(MeOH)_4]\,(ClO_4)_2$

5

Most revealing is the molecular structure of **5** (Figure 5), which was obtained by X-ray structural analysis. Complex **5** has a binuclear substructure, two mononuclear units, and a carbonate anion, which is encapsulated inside the molecule. Carbonate-containing zinc complexes of polydentate ligands are well known[9,13,19−21] and, usually, three identical metal centres are attached to the carbonate oxygen atoms. In **5** the carbonate is coordinated to four zinc ions. Furthermore, the carbonate acts as a bridging ligand linking both mononuclear units of the molecule with an oxygen atom. Two differently bound zinc ions are six-coordinated with slightly distorted octahedral geometries. One zinc ion is surrounded by the tridentate ligand L, two methanol molecules, and a carbonate oxygen. The other zinc ion is incorporated into the binuclear substructure of **5** and bears two molecules of the ligand, a methanol molecule, and a carbonate oxygen. One L acts as a bridging ligand, and only its phenolate oxygen is bound to this zinc. The remaining two zinc ions in **5** are fivefold coordinated with a different bonding. One of these zinc ions belongs to the binuclear substructure of **5**. It bears two molecules of L as well as a carbonate oxygen. It is the only zinc ion in **5** without any coordinated methanol. The geometry around this zinc can be described as highly distorted square pyramidal. Whereas

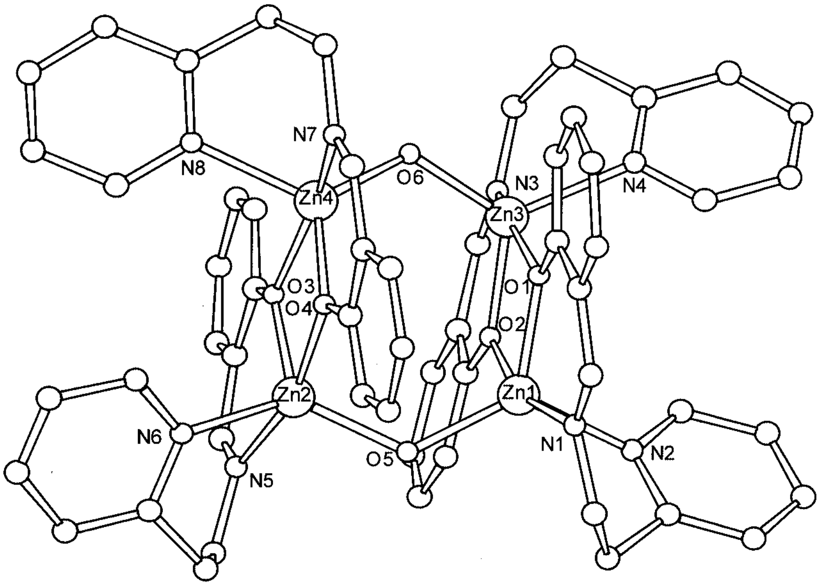

Figure 4. Coordination environments of the zinc ions in **3a** with selected bond lengths [Å] and angles [°]: Zn1−O1 2.013(5), Zn1−O2 2.109(5), Zn1−O5 1.952 (5), Zn1−N1 2.081(6), Zn1−N2 2.132(6), Zn2−O3 2.004(5), Zn2−O4 2.104(6), Zn2−O5 1.952(5), Zn2−N5 2.099(7), Zn2−N6 2.127(7), Zn3−O1 2.111(5), Zn3−O2 2.2.012(5), Zn3−O6 1.949(5), Zn3−N3 2.107(6), Zn3−N4 2.150(6), Zn4−O3 2.137(5), Zn4−O4 2.010(6), Zn4−O6 1.958(5), Zn4−N7 2.092(7), Zn4−N8 2.121(7); O1−Zn1−O2 77.4(2), O1−Zn1−O5 124.4(2), O1−Zn1−N1 89.0(2), O1−Zn1−N2 111.8(2), O2−Zn1−O5 97.4(2), O2−Zn1−N2 90.8(2), O5−Zn1−N1 98.5(2), N1−Zn1−N2 85.0(2), O3−Zn2−O5 123.1(2), O3−Zn2−O4 77.2(2), O3−Zn2−N5 90.0(2), O3−Zn2−N6 113.0(3), O4−Zn2−O5 95.7(2), O4−Zn2−N6 91.0(3), O5−Zn2−N5 99.2(2), O5−Zn2−N6 123.7(2), N5−Zn2−N6 85.3(3), O1−Zn3−O2 77.3(2), O1−Zn3−O6 96.1(2), O1−Zn3−N3 161.4(2), O1−Zn3−N4 91.4 (2), O2−Zn3−O6 120.1(2), O2−Zn3−N3 88.3(2), O2−Zn3−N4 85.5(2), O6−Zn3−N3 101.4(2), O6−Zn3−N4 119.7(2), O3−Zn4−O4 76.3(2), O3−Zn4−O6 98.1(2), O3−Zn4−N7 160.7(3), O3−Zn4−N8 91.8(2), O4−Zn4−O6 125.7(2), O4−Zn4−N7 88.0(3), O4−Zn4−N8 117.5(3), O6−Zn4−N7 100.3(3), N7−Zn4−N8 85.3(3), Zn1−O1−Zn3 102.6(2), Zn1−O2−Zn3 102.7(2), Zn1−O5−Zn2 123.6(2), Zn2−O3−Zn4 102.5(2), Zn2−O4−Zn4 103.5(2), Zn3−O6−Zn4 123.7(3)

one L molecule is bound to this zinc ion by its three donor atoms, the second one only occupies one coordination site with its phenolate oxygen. The phenolate oxygen acts as bridging atom and links the two metal centres in this substructure. The other fivefold coordinated zinc ion in **5** is the centre of a mononuclear unit and has a slightly distorted square-pyramidal geometry. The coordination sphere contains three donor atoms of L as well as a methanol oxygen and a carbonate oxygen.

Generally, the insertion of CO_2 into Zn−OH−Zn bridges does not occur. However, Karlin et al.[20] reported an exceptional case of a dinuclear zinc hydroxide complex that absorbed atmospheric carbon dioxide. Our experimental results indicate that complexes **3** and **3a** are not sufficiently reactive to bind the carbon dioxide in the coordination sphere of zinc, although it could be possible that the bonds in the Zn−OH−Zn bridges of **3** or **3a** are weakened at higher temperatures, leading to the insertion of water molecules. Complexes with the resulting Zn−OH···H_2O−Zn unit are reported to be more reactive towards CO_2 [18] and able to coordinate it as hydrogen carbonate. The last step of this reaction cascade would consist of the conversion of the hydrogen carbonate containing complex into **5**. Unfortunately we were not able to isolate any of the intermediates proposed.

Solutions of the zinc complexes of L show a remarkably intense blue fluorescence if irradiated with UV light.

Conclusion

The Schiff base L shows a great variety in its complex chemistry with zinc. The key to the successful exploitation of its synthetic potential is the smooth access to the binuclear water-containing complex **1**, which was found to be a suitable starting material for subsequent conversions. Our intention of performing enzyme-like biomimetic reactions with **1** was fulfilled in some respects. Like the resting states in zinc enzymes, **1** could be activated by deprotonation of its coordinated water molecules. The resulting hydroxide-containing complex was subjected to further conversions. Unfortunately, a complex with a highly reactive Zn-OH unit such as is found in the active form of the natural zinc enzymes has not been obtained. The OH ions in the isolated complexes of **3** and **3a** are involved in Zn−OH−Zn bridges and are significantly less reactive. Therefore, the hydroxide function in **3** was found to be unreactive towards carbon dioxide at moderate temperatures. The reaction of **3** was effected at higher temperatures but resulted in the carbonate-containing complex **5**. Thus, a complex with the Zn-OCO_2H motif has not been obtained. Nevertheless, the unique structural features of the carbonate complex **5** reveal the extraordinary synthetic capacity of L in zinc complex chemistry. One property of L is its capability to form multinuclear shell-like systems that encapsulate small molecules like carbonate.

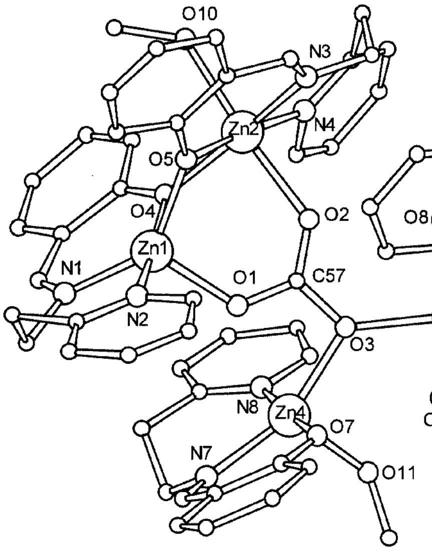

Figure 5. Molecular structure of **5** (cation only) with selected bond lengths [Å] and angles [°]: Zn1−O1 2.002(3), Zn1−O4 2.101(4), Zn1−O5 2.015(3), Zn1−N1 2.0023(4), Zn1−N2 2.146(5), Zn2−O2 2.150(3), Zn2−O4 2.114(3), Zn2−O5 2.077(4), Zn2−O10 2.166(4), Zn2−N3 2.068(4), Zn2−N4 2.133(4), Zn3−O3 2.151(3), Zn3−O6 2.040(4), Zn3−O8 2.226(4), Zn3−O9 2.111(4), Zn3−N5 2.078(4), Zn3−N6 2.172(4), Zn4−O3 2.076(3), Zn4−O7 2.034(4), Zn4−O11 2.081(4), Zn4−N7 2.010(5), Zn4−N8 2.205(5); O1−Zn1−O5 104.89(14), O1−Zn1−N1 115.36 (17), O5−Zn1−N1 138.71(17), O1−Zn1−O4 93.31(14), O5−Zn1−O4 89.88(16), O1−Zn1−N2 92.01(16), O5−Zn1−N2 94.84(16), N1−Zn1−N2 92.65(18), O4−Zn1−N2 172.47(16), O1−Zn1−Zn2 83.31(10), O5−Zn1−Zn2 42.28(10), N1−Zn1−Zn2 132.22(13), O4−Zn1−Zn2 43.53(9), N2−Zn1−Zn2 132.16(12), O5−Zn2−O4 76.99(14), N3−Zn2−O4 164.94(16), O5−Zn2−N4 175.22(15), N3−Zn2−N4 93.03(18), O4−Zn2−N4 101.92(16), O5−Zn2−O2 92.96(14), N3−Zn2−O2 89.78(15), O4−Zn2−O2 90.39(13), N4−Zn2−O2 82.37(15), O5−Zn2−O10 94.40(14), N3−Zn2−O10 89.01(16), O4−Zn2−O10 92.70(14), N4−Zn2−O10 90.30(15), O2−Zn2−O10 172.50(14), O5−Zn2−Zn1 40.75(10), N3−Zn2−Zn1 122.86(13), O4−Zn2−Zn1 43.19(10), N4−Zn2−Zn1 135.98(12), O2−Zn2−Zn1 74.01(9), O10−Zn2−Zn1 112.75(10), O6−Zn3−N5 88.50(16), O6−Zn3−O9 91.57(16), N5−Zn3−O9 101.59(16), O6−Zn3−O3 84.68(13), N5−Zn3−O3 170.44(16), O9−Zn3−O3 85.32(14), O6−Zn3−N6 178.24(17), N5−Zn3−N6 92.12(17), O9−Zn3−N6 86.69(17), O3−Zn3−N6 94.89(15), O6−Zn3−O8 98.89(15), N5−Zn3−O8 90.81(15), O9−Zn3−O8 164.01(14), O3−Zn3−O8 83.65(13), N6−Zn3−O8 82.76(15), N7−Zn4−O7 90.59(18), N7−Zn4−O3 156.59(16), O7−Zn4−O3 86.96(15), N7−Zn4−O11 109.08(17), O7−Zn4−O11 94.51(16), O3−Zn4−O11 94.33(14), N7−Zn4−N8 92.51(19), O7−Zn4−N8 175.95(17), O3−Zn4−N8 89.16(15), O11−Zn4−N8 86.92(16), N7−Zn4−O1 99.73(6), O7−Zn4−O1 95.34(15), O3−Zn4−O1 57.43(12), O11−Zn4−O1 149.39(14), N8−Zn4−O1 81.58(14)

A systematic variation of the ligand structure should enable the synthesis of hydroxide-containing zinc complexes with a higher hydrolytic reactivity than **3**.

If the Zn−OH−Zn bridges in **3** are sufficiently weakened, they might become more reactive towards CO_2 and other substrates even at ambient temperatures. With the flexibility of the ligand being maintained, a better reaction pathway of the substrate would be achieved, as for the carbonate ion in **5**. Furthermore, an additional activation of the coordinated substrate by an adjacent zinc centre in bi- or multinuclear complexes would also be advantageous. The challenge of designing zinc complexes with an enzyme-like hydrolytic activity towards carbon dioxide and amide bonds persists.

Experimental Section

Starting materials were obtained commercially and used without purification.

1: 2-(2-Aminoethyl)pyridine (1.83 g, 15 mmol) in 10 mL of methanol and salicylaldehyde (1.83 g, 15 mmol) in 15 mL of methanol were combined at ambient temperature to give a deep yellow solution. Then, zinc perchlorate hexahydrate (5.59 g, 15 mmol) in 25 mL of aqueous 90% methanol was added. The solution was warmed to 35 °C, and sodium hydroxide (0.6 g, 15 mmol) in 20 mL of methanol was added while stirring. After stirring at 35 °C, the mixture was filtered. A strong fluorescent pale-yellow solution and yellow crystals of the product were obtained. Yield 78%. $C_{28}H_{30}Cl_2N_4O_{12}Zn_2$ (816.24): calcd. C 41.20, H 3.70, Cl 8.69, N 6.86; found C 40.80, H 3.45, Cl 8.55, 7.05 N.

2: 2-(2-Aminoethyl)pyridine (1.83 g, 15 mmol) and salicylaldehyde (1.83 g, 15 mmol) were combined in 50 mL of dry methanol, and zinc perchlorate hexahydrate (5.59 g, 15 mmol) in 20 mL of dry methanol was added. After warming to 35 °C, a solution of sodium hydroxide (0.6 g, 15 mmol) in 20 mL of methanol was added while stirring. The mixture was then filtered. Yellow crystals of the product were formed from the pale-yellow fluorescent solution. Yield 75%. $C_{32}H_{42}Cl_2N_4O_{12}Zn_2$ (908.34): calcd. C 42.31, H 4.66, Cl 7.81, N 6.17; found C 41.88, H 4.87, Cl 7.69, N 5.99.

3: A solution of **1** in 100 mL of methanol freshly prepared from 2-(2-aminoethyl) pyridine (1.83 g, 15 mmol), salicylaldehyde (1.83 g, 15 mmol), zinc perchlorate hexahydrate (5.59 g, 15 mmol), and sodium hydroxide (0.6 g, 15 mmol) was heated to reflux, and sodium hydroxide (0.3 g, 7.5 mmol) was added. Whilst heating at reflux for 30 min under argon the NaOH dissolved and a product precipitated. The mixture was filtered hot, and the volume of the pale-yellow filtrate was reduced. The solution was then cooled slowly in a closed vessel. Compound **3** precipitated as large colourless crystals. Yield about 70%. $C_{56}H_{54}B_2F_8N_8O_6Zn_2$ [22] (1239.46): calcd. C 54.27, H 4.39, N 9.04; found C 54.19, H 4.35, N 9.11.

3a: A solution of **3** in 100 mL of methanol was freshly prepared from salicylaldehyde (1.83 g, 15 mmol), 2-(2-aminoethyl)pyridine (1.83 g, 15 mmol), zinc perchlorate hexahydrate (5.59 g, 15 mmol), and sodium hydroxide (0.9 g, 15 mmol). The mixture was then stirred at 60 °C for 45 min in the presence of air. The mixture was filtered hot and slowly cooled to 5 °C. Compound **3a** was obtained as large colourless crystals. Yield about 70%.[23]

Reaction of 3 with Perchloric Acid: Compound **3** (2.05 g, 1.5 mmol) was dissolved in 100 mL of methanol. 5% aqueous perchloric acid (6.03 mL, 3 mmol) was then added within a period of 10 min at room temperature. The mixture was stirred for 30 min. Crystals of **1** were obtained upon reducing the volume of the solution slowly.

Reaction of 3a with Perchloric Acid: In an analogous manner, **3a** was treated with 5% aqueous perchloric acid. Crystals of **1** were obtained upon reducing the volume of the solution slowly.

4: A solution of **1** in 100 mL of aqueous methanol freshly prepared from salicylaldehyde (1.83 g, 15 mmol), 2-(2-aminoethyl)pyridine (1.83 g, 15 mmol), zinc perchlorate hexahydrate (5.59 g, 15 mmol), and sodium hydroxide (0.6 g, 15 mmol) was heated to reflux. Then, sodium hydroxide (0.6 g, 15 mmol) was added, and the mixture was

Table 1. Crystallographic data of the complexes **1**, **2**, **3a**, **4**, and **5**

	1	**2**	**3a**	**4**	**5**
Empirical formula	$C_{28}H_{30}Cl_2N_4\ O_{12}Zn_2$	$C_{32}H_{42}Cl_2N_4O_{14}Zn_2$	$C_{57}H_{52}Cl_{1.5}N_8O_{14.4}Zn_4$ [a]	$C_{57}H_{55}ClN_8NaO_9Zn_2$	$C_{64.7}H_{79.1}Cl_2N_8O_{24.7}Zn_4$ [b]
Molecular weight	816.24	908.34	1394.12	1185.32	1696.44
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P1$	$Iba2$	$P1$
a [Å]	12.3312(4)	10.4282(8)	12.0174(8)	19.0520(5)	11.9642(8)
b [Å]	15.9495(8)	10.7218(8)	12.6098(8)	15.1148(4)	18.1471(12)
c [Å]	16.0259(8)	16.8474(13)	22.4790(14)	18.7647(5)	18.9783(12)
α [°]	90.00	90.00	87.9000(10)	90.00	82.5670(10)
β [°]	98.318(3)	93.5250(10)	77.9940(10)	90.00	86.7630(10)
γ [°]	90.00	90.00	71.0640(10)	90.00	72.0110(10)
Volume [Å^3]	3118.8(2)	1880.1(2)	3149.8(3)	5403.6(2)	3885.5(4)
Z	4	4	2	4	2
Calcd. density [g/cm^{-3}]	1.738	1.604	1.470	1.418	1.450
Absorp. coeff. [mm^{-1}]	1.781	1.490	1.636	1.006	1.367
F(000)	1664	936	1421	2388	1750
Crystal size [mm]	0.35×0.32× 0.28	0.6×0.6×0.3	0.6×0.4×0.3	0.38×0.32× 0.28	0.4×0.3×0.2
Θ-range [°]	3.05−23.29	1.96−28.28	1.71−28.33	2.14−23.28	1.70−28.29
Index-ranges	0/13	−13/+13	−16/15	−21/+21	−15/+15
	−17/17	−14/+14	−16/16	0/16	−24/+23
	−17/17	−21/+22	−29/29	−20/20	−25/+24
No. of reflections					
unique	4331	4529	15058	3786	18524
observed [$I > 2\sigma(I)$]	8331	18.984	34327	7046	42264
Parameters	480	260	810	343	969
Final R indices $R1$ [$I > 2\sigma(I)$]	0.0400	0.0243	0.0826	0.0473	0.0570
$wR2$	0.1121	0.0659	0.2747	0.1354	0.1750
Largest diff. peak/hole[e/ Å]	0.557/−0.638	0.433/−0.391	1.770/−1.441	1.207/0.794	0.980/−0.750

[a] Compound **3a** crystallizes from a mixture of 0.5 equivalents of methanol and 0.5 equivalents of water; the anions were found: 1.5 equivalents of perchlorate and 0.5 equivalents of hydrogencarbonate. [b] Compound **5** crystallizes from a mixture of 3.7 equivalents of methanol and 2 equivalents of water (OH atoms are missing in the formula).

stirred under reflux for 30 min. As the sodium hydroxide dissolved a precipitate of zinc hydroxide separated from the mixture. The precipitate was then filtered off and the filtrate was cooled slowly. Compound **4** crystallised as a colourless solid. Yield 76%. $C_{57}H_{55}ClN_8NaO_9Zn_2$ (1185.32): calcd. C 57.76, H 4.68, Cl 2.99, N 9.45; found C 57.69, H 4.65, Cl 2.67, N 9.50.

5: Salicylaldehyde (1.83 g, 15 mmol) was dissolved in 50 mL of methanol and 2-(2-aminoethyl)pyridine (1.83 g, 15 mmol) in 20 mL of methanol was added at room temperature. After 10 min, zinc perchlorate hexahydrate (5.59 g, 15 mmol) in 50 mL of methanol was added, and the mixture was heated to 60 °C. A solution of sodium hydroxide (0.90 g, 22.5 mmol) in 50 mL of methanol was added and a cloudy mixture was obtained. Then, a stream of carbon dioxide was passed through the mixture for 45 min at 60 °C; most of the reaction products dissolved. The remaining undissolved solid was filtered off and the filtrate was cooled in a closed flask to 0 °C under a CO_2 atmosphere. After a few days, compound **5** crystallised as a colourless solid. Yield 55%. $C_{61}H_{68}Cl_2N_8O_{19}Zn_4 \cdot 3.7CH_3OH \cdot 2.5\ H_2O$ (1713.27): calcd. C 45.36, H 5.17, Cl 4.14, N 6.54; found C 45.77, H 4.76, Cl 4.32, N 6.88.

X-ray Crystallographic Study: Data for complexes **1** and **4** were collected on a NONIUS Kappa CCD diffractometer (Mo-K_α, λ = 0.71073 Å, and ω scans), at 183 K, up to Θ = 27.44°. The structures were solved by direct methods (refinement by least-squares against F^2, SHELX program[24]). Diffraction data for the complexes **2**, **3**, **3a**, and **5** were recorded at 200 K with a Siemens SMART 1000 CCD diffractometer fitted with a molybdenum tube (Mo-K_α, λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined anisotropically with the SHELX program. The structural parameters were refined against F^2. Figures were produced with the winray program.[25] Table 1 lists the crystallographic data[26] of the complexes **1**, **2**, **3a**, **4**, and **5**.

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[22] Because of experimental problems (ClO_4^- counterion), an elementary analysis of **3** could not be performed. The results of the elementary analysis of a complex with an identical cation, but with BF_4^- as counterion, are presented.

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[26] CCDC-175934 (**1**), -175955 (**2**), -1785957 (**3a**), -175935 (**4**) and -175956 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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