

## A Dinuclear Zinc Hydroxide Complex which traps Atmospheric Carbon Dioxide: Formation of a Tri-zinc Complex with a Triply Bridging Carbonate Group

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Dinuclear di- $\mu$ -hydroxo zinc(II) complex **1**, containing a tetradentate nitrogen ligand, readily absorbs atmospheric CO<sub>2</sub> to form tri-zinc complex **2**, containing an uncommon triply bridging carbonate group; the structures of **1** and **2** have been established by X-ray crystallography.

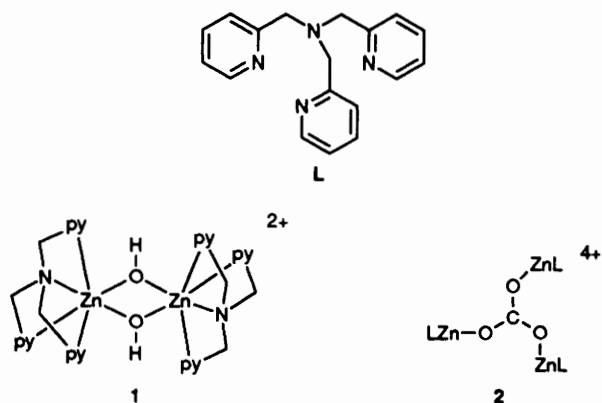
As part of our studies in biomimetic copper chemistry,<sup>1</sup> the tetradentate ligand **L** has found considerable utility, in part owing to its ability to form five-coordinate Cu<sup>II</sup> complexes, with ligation from one exogenous neutral or anionic ligand, *e.g.*, [LCu<sup>II</sup>-D]<sup>2+</sup> (D = H<sub>2</sub>O<sup>2,3</sup> or MeCN<sup>3</sup>), [LCu<sup>II</sup>-X]<sup>+</sup> (X = halide, pseudohalide)<sup>3,4</sup> or [LCu<sup>II</sup>-X'-Cu<sup>II</sup>L]<sup>2+</sup> (X' = O<sub>2</sub><sup>2-</sup>), CO<sub>3</sub><sup>2-</sup>).<sup>5,6</sup> We have recently also examined Zn<sup>II</sup> complexes

with this ligand, since aqueous solution studies have already established that LCu<sup>II</sup>-H<sub>2</sub>O and LZn<sup>II</sup>-H<sub>2</sub>O complexes form the corresponding LM-OH<sup>-</sup> analogues at rather low pH values, *e.g.*, 7.4 and 8.0 respectively.<sup>7</sup> Zinc(II) hydroxide entities are important as nucleophiles, in biological peptide amide hydrolysis (*e.g.* carboxypeptidase),<sup>8</sup> hydrolysis of carboxylic and phosphate ester substrates,<sup>9,10</sup> and in the

hydration of CO<sub>2</sub> in carbonic anhydrase<sup>11</sup> or its model compounds.<sup>12</sup> The reaction chemistry of CO<sub>2</sub> with metal hydroxides is particularly interesting since CO<sub>2</sub> is a combustion product and environmental pollutant, yet it is also a potentially useful carbon source.<sup>13</sup> Here, we describe a new di- $\mu$ -hydroxo di-zinc(II) complex with L, [LZn-( $\mu$ -OH)<sub>2</sub>-ZnL]<sup>2+</sup> **1** (py = 2-pyridyl),<sup>14</sup> which has a great affinity for atmospheric carbon dioxide, readily extracting it from the air, forming an unusual triply bridging carbonate tri-zinc(II) product [(LZn)<sub>3</sub>(CO<sub>3</sub>)]<sup>4+</sup> **2**.

Treatment of zinc perchlorate and L in methanol with 1 equiv. of KOH, under argon, gave a colourless crystalline solid [LZn-( $\mu$ -OH)<sub>2</sub>-ZnL]<sup>2+</sup> **1** in nearly quantitative yield, characterized by a strong IR absorption at 3640 cm<sup>-1</sup>, assigned to an O-H vibration.† The complex is very reactive towards air (*vide infra*), but recrystallization from an acetone-methanol mixture under argon gave colourless crystals suitable for X-ray diffraction.‡ The centrosymmetric dinuclear structure with bridging OH<sup>-</sup> groups is illustrated in Fig. 1. Each Zn<sup>II</sup> ion possesses a distorted octahedral coordination with ligation by four L nitrogen and two hydroxide O atoms. The pyridine groups containing N(3) and N(4') [as well as N(4) and N(3')] are stacked in a staggered manner, with the shortest ring-ring distance being 3.243(9) Å.

When a solution (MeOH, MeNO<sub>2</sub> or H<sub>2</sub>O) of **1** is exposed to air, CO<sub>2</sub> is readily absorbed, forming the carbonate



† In a typical reaction, L (0.26 g) dissolved in methanol (15 ml) was introduced to Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.33 g) under argon to form a colourless solution. Addition of KOH (50 mg) in MeOH (5 ml) precipitated KClO<sub>4</sub> and, after stirring for 15 min, the solution was filtered and concentrated to give colourless [LZn-( $\mu$ -OH)<sub>2</sub>-ZnL](ClO<sub>4</sub>)<sub>2</sub>, **1**(ClO<sub>4</sub>)<sub>2</sub> (0.38 g, 90% yield). <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, 300 MHz):  $\delta$  4.30 (s, 6H), 7.59 (m, 6H), 8.07 (m, 3H) and 8.92 (d, 3H). Satisfactory C, H and N elemental analyses were obtained.

‡ Crystal data: **1**(ClO<sub>4</sub>)<sub>2</sub>:  $M = 944.4$ , monoclinic,  $a = 9.814(6)$ ,  $b = 13.013(6)$ ,  $c = 15.928(4)$  Å,  $\beta = 98.35(3)^\circ$ ,  $V = 2013(2)$  Å<sup>3</sup>, space group  $P2_1/a$ ,  $Z = 4$ ,  $F(000) = 1936$ ,  $D_c = 1.42$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 14.18$  cm<sup>-1</sup>; 3948 reflections collected, of these 3717 were unique and 2068 [ $I \geq 3\sigma(I)$ ] were used in the analysis;  $R = 0.064$ ,  $R_w = 0.082$ . **2**: X-Ray-quality crystals of [(LZn)<sub>3</sub>(CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O were obtained from water.  $M = 1543.07$ , orthorhombic,  $a = 20.588(4)$ ,  $b = 21.598(5)$ ,  $c = 14.393(4)$  Å,  $V = 6400(3)$  Å<sup>3</sup>, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $F(000) = 3152$ ,  $D_c = 1.44$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 13.91$  cm<sup>-1</sup>; 6222 reflections collected, of these 3311 [ $I \geq 3\sigma(I)$ ] were used in the analysis;  $R = 0.063$ ,  $R_w = 0.076$ .

The data were collected at room temperature ( $3.5 \leq 2\theta \leq 50^\circ$ ) on a Rigaku AFC6S diffractometer using Mo-K $\alpha$  ( $\lambda = 0.71069$  Å) radiation. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods and hydrogen atoms were included at calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

complex [(LZn)<sub>3</sub>(CO<sub>3</sub>)]<sup>4+</sup> **2** in good yield.§ Bubbling CO<sub>2</sub> (g) through a nitromethane solution of **1** immediately produced **2**, as determined by <sup>1</sup>H NMR spectroscopy,†§ showing that the carbonate group in **2** is indeed derived from CO<sub>2</sub> in the aerobic

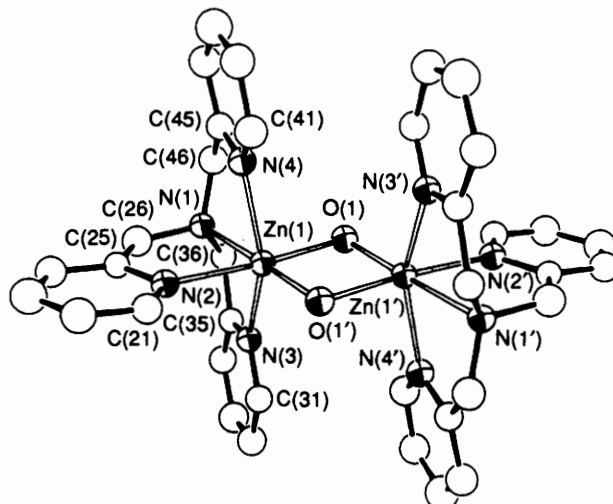


Fig. 1 ORTEP view of cationic portion of [LZn-( $\mu$ -OH)<sub>2</sub>-ZnL](ClO<sub>4</sub>)<sub>2</sub>, **1** = (ClO<sub>4</sub>)<sub>2</sub>. Selected bond distances (Å) and angles ( $^\circ$ ): Zn-O(1), 2.048(5); Zn-O(1'), 1.962(1); Zn-N(1), 2.258(7); Zn-N(2), 2.179(7); Zn-N(3), 2.195(7); Zn-N(4), 2.200(8); Zn...Zn', 2.992(1); O(1)-Zn-N(1), 97.2(2); O(1)-Zn-N(2), 175.0(3); O(1)-Zn-N(3), 92.2(2); O(1)-Zn-N(4), 93.5(2); O(1)-Zn-O(1'), 83.5(2); N(1)-Zn-N(2), 78.4(3); N(1)-Zn-N(3), 74.9(3); N(1)-Zn-N(4), 76.2(3); N(1)-Zn-O(1'), 178.7(2); N(2)-Zn-N(3), 88.8(3); N(2)-Zn-N(4), 83.3(3); N(2)-Zn-O(1'), 101.0(2); N(2)-Zn-O(1'), 104.0(2); N(3)-Zn-N(4), 151.1(3); N(4)-Zn-O(1'), 104.8(2); Zn-O(1)-Zn', 96.5(2).

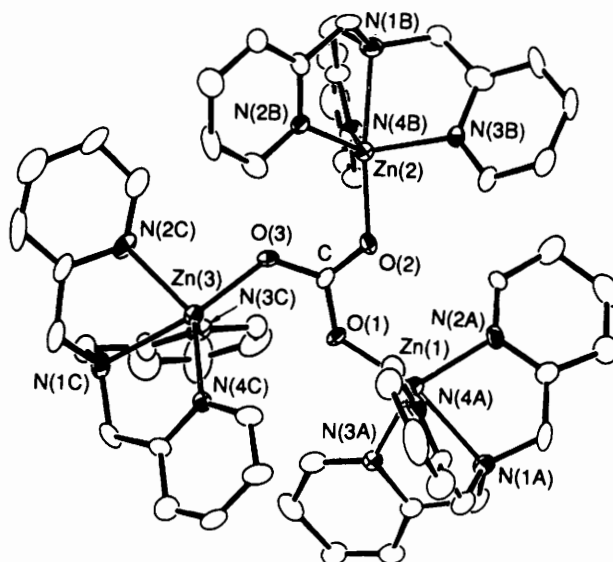


Fig. 2 ORTEP view of cationic portion of [(LZn)<sub>3</sub>(CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O, **2** = (ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O. Selected bond distances (Å) and angles ( $^\circ$ ): Zn(1)-O(1), 1.965(11); Zn(2)-O(2), 1.951(12); Zn(3)-O(3), 1.983(13); Zn(1)-N(1A), 2.225(15); Zn(2)-N(1B), 2.213(14); Zn(3)-N(1C), 2.256(16); Zn-N(2), 2.033(14)-2.103(16); Zn-N(3), 2.077(14)-2.122(16); Zn-N(4), 2.077(14)-2.127(16); Zn(1)...Zn(2), 5.087(3); Zn(2)...Zn(3), 5.038(3); Zn(1)...Zn(3), 4.884(3); C-O(1), 1.308(19); C-O(2) and C-O(3), 1.278(19); O(1)-Zn-N(1), 164.9(5)-172.2(5); N(2)-Zn-N(3), 110.2(6)-125.3(6); N(2)-Zn-N(4), 107.0(6)-124.2(6); N(3)-Zn-N(4), 109.9(6)-124.2(6).

§ In a typical reaction, **1** (0.15 g) dissolved in nitromethane (5 ml) was exposed to air. After 2-3 days colourless crystals of [(LZn)<sub>3</sub>(CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>4</sub>, **2**(ClO<sub>4</sub>)<sub>2</sub>, appeared (0.14 g, 46% yield). <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, 300 MHz):  $\delta$  4.45 (s, 6H), 7.19 (m, 3H), 7.2 (m, 3H), 8.02 (m, 3H) and 8.89 (d, 3H). Molar conductance ( $\Lambda_M$ , MeNO<sub>2</sub>): 355  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 4:1 electrolyte. Satisfactory C, H and N elemental analyses were obtained.

reaction (*vide supra*). The carbonate related IR vibrational frequencies occur at 1610, 1377 and 765  $\text{cm}^{-1}$  and the structure of **2** was established in an X-ray diffraction study, Fig. 2.‡ Trinuclear complex **2** possesses pseudo-three-fold molecular symmetry. The  $\mu_3\text{-CO}_3^{2-}$  group exhibits an uncommon coordination mode, bridging the three  $\text{Zn}^{\text{II}}$  ions through the three O atoms.<sup>15</sup> As is found for most  $\text{Cu}^{\text{II}}$  complexes with L,<sup>3-6</sup> each zinc is five-coordinate, although the geometry about Zn(1) is more distorted from trigonal bipyramidal. The carbonate group is planar and the zinc ions deviate from this plane by 0.23, 0.66 and 0.34 Å, respectively.

The formation of **2** is interesting because of the efficiency of **1** in fixing the very low concentrations of  $\text{CO}_2$  found in the atmosphere, and the novel coordination mode of the carbonate group in this zinc complex; most carbonates are monodentate, chelating or bridged *dinuclear* species.<sup>6,12,13,16</sup> While reactions of M-OH complexes with  $\text{CO}_2$  are common, examples exhibiting rapid  $\text{CO}_2$  removal from *air* are limited,<sup>16</sup> and unusual for zinc. A related notable recent study by Parkin and Vahrenkamp<sup>12</sup> shows that a  $\text{L}'\text{Zn}(\text{OH})$  complex [ $\text{L}' =$  an alkyl substituted tris(pyrazolyl)-hydroborato ligand] combines reversibly with  $\text{CO}_2$  giving a hydrogen carbonate product; this subsequently reacts further giving a  $\mu$ -carbonato di-zinc(II) compound. Complex **2** may also represent a structural model<sup>14</sup> for phosphatases such as phospholipase C from *Bacillus cereus*, where the three O atoms of  $\text{PO}_4^{3-}$  bind to the tri-zinc cluster in the enzyme active site in a manner similar to that observed in **2**.<sup>17</sup> Further studies of the reactivity of M-OH complexes with L and related ligands are in progress.

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