

Copper(II) and Zinc(II) Macrocyclic Complexes with High Efficiency in Fixing CO₂. Crystal Structures of {[ZnL]₃(μ₃-CO₃)}·(ClO₄)₄ and {[CuL]₃(μ₃-CO₃)}·(ClO₄)₄ (L = [15]aneN₃O₂)

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The Zn^{II} and Cu^{II} complexes with the macrocyclic ligand [15]aneN₃O₂ (L) readily trap atmospheric CO₂ to form the {[ZnL]₃(μ₃-CO₃)}·(ClO₄)₄ and {[CuL]₃(μ₃-CO₃)}·(ClO₄)₄ complexes, which both contain a triply bridging carbonate anion.

A number of L-Zn^{II}-H₂O and L-Cu^{II}-H₂O complexes, where L is a synthetic ligand, have been used in biomimetic zinc¹ and copper chemistry.² In particular, the metal-bound water molecule plays a fundamental role in hydrolytic mechanisms, such as hydrolysis of activated esters or phosphate esters,^{3,4} as well as in CO₂ hydration.^{5,6} The catalytic activity rests in strongly nucleophilic L-M^{II}-OH functions, generated from H₂O-bound Zn^{II} or Cu^{II} complexes.

The macrocyclic ligand [15]aneN₃O₂⁷ (L) binds Cu^{II} and Zn^{II} in aqueous solution. The species present in solution for the systems L/Cu^{II} and L/Zn^{II} and the correspondent stability constants have been potentiometrically determined.[†] In both systems, mono-hydroxo [ZnLOH]⁺ and [CuLOH]⁺ species are present at alkaline pH. In the case of Cu^{II} a dihydroxo [CuL(OH)₂] complex is also found. Aqueous and methanolic solutions containing such hydroxo complexes have a great

affinity for atmospheric CO₂, readily extracting it from the air.

When CO₂-free aqueous solutions containing equimolar amounts of L and Zn(ClO₄)₂·6H₂O or Cu(ClO₄)₂·6H₂O at pH 8.5–10 (in this pH range the [ZnLOH]⁺ or [CuLOH]⁺ species are present in large amounts in water solution) are exposed to air, CO₂ is rapidly absorbed (15–30 min), forming the products {[ZnL]₃(μ₃-CO₃)}·(ClO₄)₄ **A** or {[CuL]₃(μ₃-CO₃)}·(ClO₄)₄ **B** in good yields.[‡]

Compounds **A** and **B** are isomorphous and their molecular structures, determined by X-ray analysis (Fig. 1),[§] show the μ₃-CO₃²⁻ anion bridging the three metal ions through the three oxygens of the carbonate group. Both **A** and **B** possess threefold molecular symmetry with the metal atoms five-coordinated by the three nitrogens and one oxygen of the macrocycle and by one oxygen of the carbonate group. The metal centres are shifted from the carbonate plane in **A** and **B** by 0.189(2) and 0.294(1) Å, respectively. As shown in Fig. 1, the two trinuclear complex cations have a similar overall structure. On the other hand, there are significant differences in the coordination geometry of the metal ions. While in **A** the Zn^{II} ion assumes a distorted trigonal bipyramidal arrangement, in **B** the coordination environment of the Cu^{II} can be described as a rather distorted square pyramid. The apical position is occupied by the weakly bound ethereal O(9) atom. The Cu–O(9) bond forms an

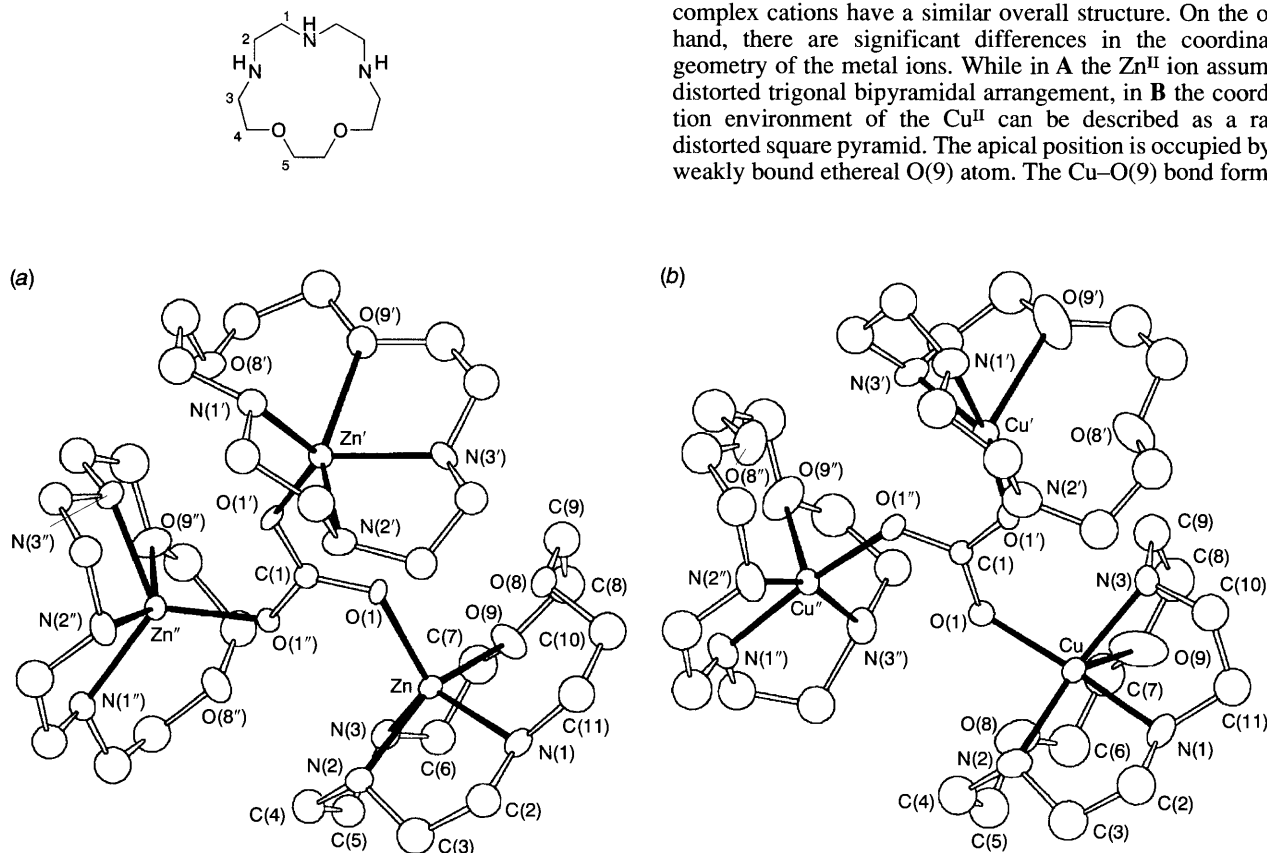


Fig. 1 (a) ORTEP drawing of the {[ZnL]₃(μ₃-CO₃)}⁴⁺ cation. Symmetry transformations: (') -y + 2, x - y + 1, z; (") -x + y + 1, -x + 2, z. Selected bond distances (Å) and angles (°): Zn–O(1) 1.946(8), Zn–N(3) 2.101(12), Zn–N(1) 2.127(12), Zn–N(2) 2.185(13), Zn–O(9) 2.337(10); O(1)–Zn–N(3) 115.5(4), O(1)–Zn–N(1) 121.1(4), N(1)–Zn–N(3) 123.0(5), O(1)–Zn–N(2) 102.5(4), N(3)–Zn–N(2) 81.8(5), N(1)–Zn–N(2) 80.7(5), O(1)–Zn–O(9) 103.7(4), N(3)–Zn–O(9) 72.4(4), N(1)–Zn–O(9) 99.2(5), N(2)–Zn–O(9) 149.2(5). (b) ORTEP drawing of the {[CuL]₃(μ₃-CO₃)}⁴⁺ cation. Symmetry transformation: (') 2 - y, x - y + 1, z; (") 1 - x + y, 2 - x, z. Selected bond distances (Å) and angles (°): Cu–O(1) 1.935(7), Cu–N(1) 1.989(10), Cu–N(3) 2.034(10), Cu–N(2) 2.058(11), Cu–O(9) 2.531(13); O(1)–Cu–N(1) 168.9(4), O(1)–Cu–N(3) 99.1(3), N(1)–Cu–N(3) 83.8(5), O(1)–Cu–N(2) 90.4(4), N(1)–Cu–N(2) 83.2(5), N(3)–Cu–N(2) 157.3(5), O(9)–Cu–N(3) 69.9(5), O(8)–Cu–O(9) 62.1(5), O(1)–Cu–O(9) 101.0(5), N(1)–Cu–O(9) 90.1(6), N(2)–Cu–O(9) 128.6(4).

angle of $29.4(4)^\circ$ with the normal to the basal plane formed by N(1), N(2), N(3) and O(1).

Similarly coordinated carbonate has rarely been observed in Cu^{II} or Zn^{II} complexes.⁹ In the latter case, Murthy and Karlin reported a dinuclear di- μ -hydroxo zinc(II) complex, containing a tetradentate nitrogen ligand, which absorbs CO_2 to form a trizinc complex containing a triply bridging carbonate group. In the present case, both Zn^{II} and Cu^{II} complexes absorb atmospheric CO_2 to give analogous triply bridging carbonate complexes. Both complexes exhibit a high efficiency in fixing the very low concentrations of CO_2 found in the atmosphere. While fixation of CO_2 by transition metal complexes is common, only a few examples of CO_2 uptake from the air have been reported.^{9,10} In these cases the CO_2 fixation occurs in a few days or in several hours. The present complexes with [15]ane N_3O_2 can trap carbon dioxide in a few tens of minutes both in water and in methanolic solutions.

It is worth noting that methanolic solutions containing **L** and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of 1 equiv. of base absorb CO_2 from the air. Even from these solutions the $\{[\text{ZnL}]_3(\mu_3\text{-CO}_3)\} \cdot (\text{ClO}_4)_4$ or $\{[\text{CuL}]_3(\mu_3\text{-CO}_3)\} \cdot (\text{ClO}_4)_4$ complexes crystallize in 15–30 min.‡ In the case of the Zn^{II} complexes, ¹H NMR spectra carried out on a methanolic solution containing **L**, Zn^{II} and NaOH in equimolar ratios show analogous spectral features with respect to those recorded for aqueous solutions containing the $[\text{ZnLOH}]^+$ species (pD 10),¶ thus suggesting the presence of such a hydroxo complex in methanol also.

The formation of **L**-M-OH species seems to play a fundamental role in the process of hydration and fixing of CO_2 . Most likely, the metal-bound hydroxo ion combines with CO_2 to produce a hydrogen carbonate complex. Recently, Parkin and coworkers⁶ have found that an $\text{L}_1\text{-Zn-OH}$ complex combines reversibly with CO_2 giving a hydrogen carbonate adduct which can further react to form a μ -carbonato dizinc complex. A similar stepwise mechanism, which considers the formation of a **L**-M- HCO_3 complex and its subsequent reaction with **L**-M-OH species, can be suggested to explain the assembly of the **A** and **B** trinuclear complexes.

Further studies on CO_2 hydration process by complexes with [15]ane N_3O_2 are in progress.

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Footnotes

† Stability constants of the Cu^{II} and Zn^{II} complexes with **L** (0.15 mol dm⁻³ NaCl aqueous solution, 298.1 K): $\text{Cu}^{2+} + \text{L} = [\text{CuL}]^{2+}$, $\log K = 15.51$; $[\text{CuL}]^{2+} + \text{OH}^- = [\text{CuLOH}]^+$, $\log K = 4.72(4)$; $[\text{CuLOH}]^+ + \text{OH}^- = [\text{CuL}(\text{OH})_2]$, $\log K = 2.69$; $\text{Zn}^{2+} + \text{L} = [\text{ZnL}]^{2+}$, $\log K = 8.95(2)$; $[\text{ZnL}]^{2+} + \text{OH}^- = [\text{ZnLOH}]^+$, $\log K = 4.92(4)$. Ligand and metal concentrations 1×10^{-3} mol dm⁻³. For method and procedure used see ref. 11. The stability constants for the $[\text{ML}]^{2+}$ complexes are in good accord with those found by Hancock *et al.*⁷

‡ In a typical experiment a CO_2 -free 0.05 mol dm⁻³ aqueous solution of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added to an equimolar aqueous solution of **L**. The pH of these solutions was adjusted to 9.5 by addition of NaOH. After 15–30 min colourless crystals of **A** (63% yield) or blue crystals of **B** (59% yield) were formed. The same reactions, performed in CO_2 -free methanolic solutions in the presence of 1 equiv. of NaOH, gave the products **A** and **B** in higher yields (78% and 73% for **A** and **B**, respectively). Crystals suitable for X-ray analysis with the same crystallographic cells were obtained from both solvents. Satisfactory C, H, and N elemental analyses were obtained.

§ Crystal data for $\{[\text{ZnL}]_3(\mu_3\text{-CO}_3)\} \cdot (\text{ClO}_4)_4$ **A**: $\text{C}_{31}\text{H}_{69}\text{Cl}_4\text{N}_9\text{O}_{25}\text{Zn}_3$, $M_w = 1305.86$, prismatic colourless crystals (approximate dimensions $0.03 \times 0.2 \times 0.25$ mm), rhombohedral space group $R\bar{3}c$, with $a, b = 22.300(5)$, $c = 17.980(8)$ Å, $V = 7743(4)$ Å³, $Z = 6$, $D_c = 1.680$ Mg m⁻³, $F(000) = 4056$, $\mu(\text{Mo-K}\alpha) = 1.680$ mm⁻¹. For $\{[\text{CuL}]_3(\mu_3\text{-CO}_3)\} \cdot (\text{ClO}_4)_4$ **B**: $\text{C}_{31}\text{H}_{69}\text{Cl}_4\text{Cu}_3\text{N}_9\text{O}_{25}$, $M_w = 1300.37$, prismatic blue crystals (approximate dimensions $0.2 \times 0.34 \times 0.5$ mm), rhombohedral, space group $R\bar{3}c$, with $a, b = 22.292(7)$, $c = 18.096(8)$ Å, $V = 7788(5)$ Å³, $Z = 6$, $D_c = 1.664$ Mg m⁻³, $F(000) = 4038$, $\mu(\text{Mo-K}\alpha) = 1.513$ mm⁻¹.

1583 Reflections ($2.5 < \theta < 25^\circ$, $\theta\text{-}2\theta$, T 298 K) for **A** and 1592 ($3 < \theta < 25^\circ$, $\theta\text{-}2\theta$, T 298 K) for **B** were measured on an Enraf-Nonius CAD4 X-ray diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71069$ Å). R [reflections with $I > 2\sigma(I)$] = 0.0666 and 0.0598 for **A** and **B**, respectively; $wR^2 = 0.1719$ and 0.1611 for **A** and **B**, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ ¹H NMR: (D_2O solution, pD 10) δ 2.58 (m, 4H, H-1), 2.94 (m, 4H, H-2), 3.00 (m, 4H, H-3), 3.70 (m, 4H, H-4), 3.80 (s, 4H, H-5); (MeOD solution, Zn^{II} , **L** and NaOH in equimolar ratio) δ 2.67 (m, 4H, H-1), 3.00 (m, 4H, H-2), 3.05 (m, 4H, H-3), 3.75 (m, 4H, H-4), 3.80 (s, 4H, H-5).

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