DALTON COMMUNICATION

A new carbonate bridged tetranuclear zinc(II) complex of an asymmetric tetrapodal compartmental ligand

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A zinc(II) complex of the asymmetric tetrapodal proligand 2-{[bis(2-pyridinylmethyl)amino]methyl}-6-[{[(2-hydroxyphenyl)methyl](2-pyridinylmethyl)amino}methyl]-4-methylphenol reacts with carbon dioxide to give the tetranuclear zinc(II) complex $[Zn_4L_2(CO_3)](BF_4)_2{\cdot}5CH_3OH{\cdot}4H_2O$; the crystal structure of this complex revealed an unusual μ_3-binding mode of the carbonate to one mononuclear zinc atom and a dinuclear pair of zinc atoms.

The nucleophilic fixation of carbon dioxide by hydroxo metal complexes to afford metal carbonato species is relevant to the structure and function of metalloenzymes such as carbonic anhydrase.[1] It is also of interest from the viewpoint of environmental chemistry as an understanding of the reaction may lead to a practical method for the controlled removal of carbon dioxide from the atmosphere.[2–5] Studies on the fixation of carbon dioxide by mononuclear zinc complexes and several carbonate binding modes have been structurally characterised (Fig. 1: a,[6–11] b,[12–15] c,[16] d [12,13,17]). In the present work utilising dinuclear zinc complexes of compartmental ligands an unusual variant on the μ_3-binding mode of the carbonate anion has been structurally identified.

The donor asymmetric compartmental proligand 2-{[bis(2-pyridinylmethyl)amino]methyl}-6-[{[(2-hydroxyphenyl)methyl]-(2-pyridinylmethyl)amino}methyl]-4-methylphenol (H_2L), was synthesised by the reaction of 2,6-bis(chloromethyl)-4-methylphenol,[18] 2-{[(2-pyridinylmethyl)amino]methyl}phenol,[19] and *N*,*N*-bis(2-pyridylmethyl)amine[20] in a 1 : 1 : 1 ratio in THF in the presence of triethylamine.[21] Reaction of H_2L with two equivalents of hydrated $Zn(BF_4)_2$ in methanol, also in the presence of two equivalents of triethylamine, gave colourless crystals of complex **1**.† X-Ray structural analysis‡ revealed that a tetranuclear zinc(II) complex had been formed having the formula $[Zn_4L_2(CO_3)](BF_4)_2{\cdot}5CH_3OH{\cdot}4H_2O$ [the bulk sample of **1** analysed as $[Zn_4L_2(CO_3)](BF_4)_2{\cdot}2CH_3OH{\cdot}3H_2O$ and it is likely that molecules of solvent were lost on standing].†

The molecular structure of the dication from **1** is shown in Fig. 2 with selected bond lengths and angles given in the caption. The tetranuclear core of the cation is detailed in Fig. 3. The structure comprises two dinuclear $[Zn_2L]$ units which are joined to each other by the bridging pendant phenolato oxygen atoms O(2) and O(2A). The complexes are further bridged by a

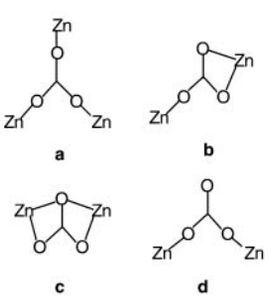
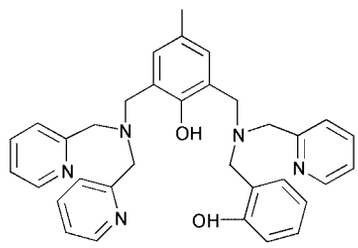


Fig. 1 Binding modes for the bridging carbonate anion in di- and trinuclear Zn complexes.



H_2L

μ_3-carbonato group and it is the associated connectivity which is unusual. Two oxygen atoms from the carbonate anion bridge a dinuclear centre assembled by ligand coordination whereas in previous examples of μ_3-bridging each Zn atom was independent of the others in the molecule.[6–11] The complex cation may be regarded as arising from the self assembly of two dinuclear components (Fig. 4).

The first component [Zn(1)Zn(2)L] is donor set asymmetric. Both Zn atoms are five-coordinate with Zn(1) having an N_3O_2 donor set and Zn(2) an N_2O_3 donor set. The degrees of trigonality (τ) for these centres are 0.47 and 0.71 respectively showing that Zn(2) is distorted towards trigonal bipyramidal geometry ($\tau = 1$) whereas Zn(1) is intermediate between trigonal bipyramidal (*TBPY*) and square pyramidal (*SPY*) geometry ($\tau = 0$).[22] Zn(1) is bound by a tertiary nitrogen atom N(1), two pyridyl nitrogen atoms N(2), N(3), a bridging cresolato oxygen atom O(1) [to Zn(2)] and an oxygen atom from the μ_3-carbonate (O5). The Zn–amine N distance (2.29 Å) is larger than the Zn–pyridyl N distances (average 2.10 Å) whilst the Zn–O distances are both *ca.* 2.00 Å. Zn(2) is symmetrically bridged to Zn(1) by O(1) and non-symmetrically to Zn(2A) by the two pendant phenolato oxygen atoms O(2) and O(2A) and further coordinated to the tertiary nitrogen atom N(4) and the pyridyl nitrogen atom N(5).

The second component [Zn(1A)Zn(2A)L] is coordination number asymmetric with Zn(1A) five-coordinate and Zn(2A) six-coordinate. The metals are bridged by the cresolato oxygen atom of the ligand O(1A) and by two *syn–syn* oxygen atoms, O(3) and O(4), from the μ_3-carbonate. The degree of trigonality (τ) for this centre is 0.63 indicating a geometry intermediate between the *TBPY* and *SPY* geometries. Zn(1A) has an N_3O_2 donor set in which the Zn–amine N interaction (2.26 Å) is longer than the Zn–pyridyl N interactions (average 2.08 Å). Zn(2A) is six-coordinate with an N_2O_4 donor set. It is doubly bridged to Zn(1A) by O(1A) and the *syn–syn* carbonate, and to Zn(2) by the bis-phenolato bridge described above. The two N donor atoms are derived from the tertiary amine N(4A) and pendant pyridyl N(5A) nitrogen atoms. The *trans*-axial angles of 170.8 [O(1A)–Zn(2A)–O(2A)], 173.3 [O(2)–Zn(2A)–N(4A)] and 162.0° [O(4)–Zn(2A)–N(5A)] indicate a distorted octahedral geometry.

The intermetallic separations reflect the nature of the bridges. The singly bridged (μ_1) Zn(1)···Zn(2) distance is 3.55 Å and the bridging angle [Zn(1)–O(1)–Zn(2)] is 126.3°.§ The doubly bridged (μ_1, $\mu_{2\ syn-syn}$) Zn(2A)···Zn(1A) distance is

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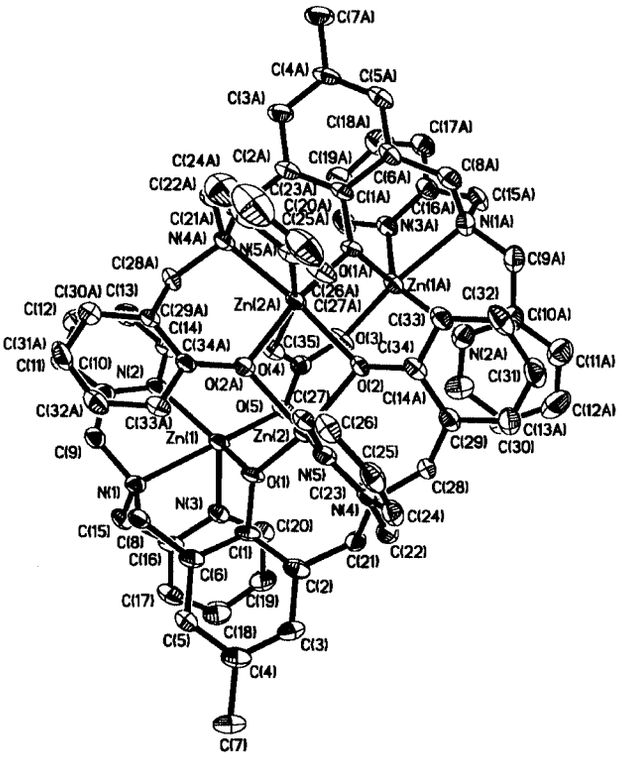


Fig. 2 An ORTEP drawing of the molecular structure of the dication $[Zn_4L_2(CO_3)]^{2+}$ showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. The designations Zn(1A), Zn(2A), C(1A) *etc.* do not imply symmetry generated atoms in this particular structure. Selected bond lengths (Å) and angles (°) at the zinc(II) atoms: Zn(1)–O(1) 2.008(4), Zn(1)–O(5) 1.999(4), Zn(1)–N(1) 2.287(5), Zn(1)–N(2) 2.098(5), Zn(1)–N(3) 2.092(5), Zn(2)–O(1) 1.975(4), Zn(2)–O(2) 2.006(4), Zn(2)–O(2A) 2.041(4), Zn(2)–N(4) 2.192(5), Zn(2)–N(5) 2.078(5), Zn(1A)–O(1A) 2.003(4), Zn(1A)–O(3) 1.974(4), Zn(1A)–N(1A) 2.262(5), Zn(1A)–N(2A) 2.067(6), Zn(1A)–N(3A) 2.091(5), Zn(2A)–O(1A) 2.022(4), Zn(2A)–O(2A) 2.070(4), Zn(2A)–O(2) 2.076(4), Zn(2A)–O(4) 2.178(4), Zn(2A)–N(4A) 2.134(5), Zn(2A)–N(5A) 2.245(5), Zn(1)–Zn(2) 3.5530(10), Zn(1A)–Zn(2A) 3.4504(10), Zn(2)–Zn(2A) 3.0454(10); N(1)–Zn(1)–O(5) 168.99(17), N(3)–Zn(1)–N(2) 110.73(19), N(3)–Zn(1)–O(1) 99.32(18), O(1)–Zn(1)–N(2) 140.66(19), N(1A)–Zn(1A)–O(3) 169.21(19), N(3A)–Zn(1A)–O(1A) 105.89(19), N(2A)–Zn(1A)–N(3A) 115.1(2), N(2A)–Zn(1A)–O(1A) 131.54(19), N(4)–Zn(2)–O(2A) 174.52(17), N(5)–Zn(2)–O(2) 100.29(17), O(2)–Zn(2)–O(1) 131.55(17), O(1)–Zn(2)–N(5) 127.79(17), O(2)–Zn(2A)–N(4A) 173.29(16), N(5A)–Zn(2A)–O(1A) 101.96(16), O(1A)–Zn(2A)–O(4) 93.83(16), O(4)–Zn(2A)–O(2A) 80.35(16), O(2A)–Zn(2A)–N(5A) 84.96(16), Zn(1)–O(1)–Zn(2) 126.25(19), Zn(2)–O(2A)–Zn(2A) 95.59(17), Zn(2)–O(2)–Zn(2A) 96.50(17), Zn(2A)–O(1A)–Zn(1A) 118.02(19).

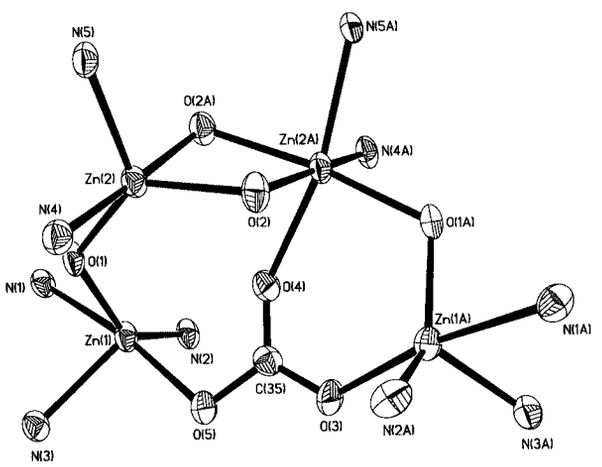


Fig. 3 The tetranuclear core of complex **1** showing the carbonate bridge.

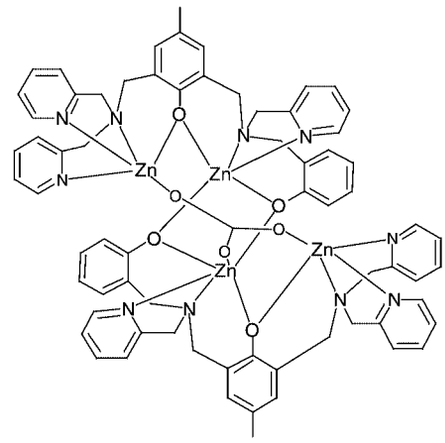
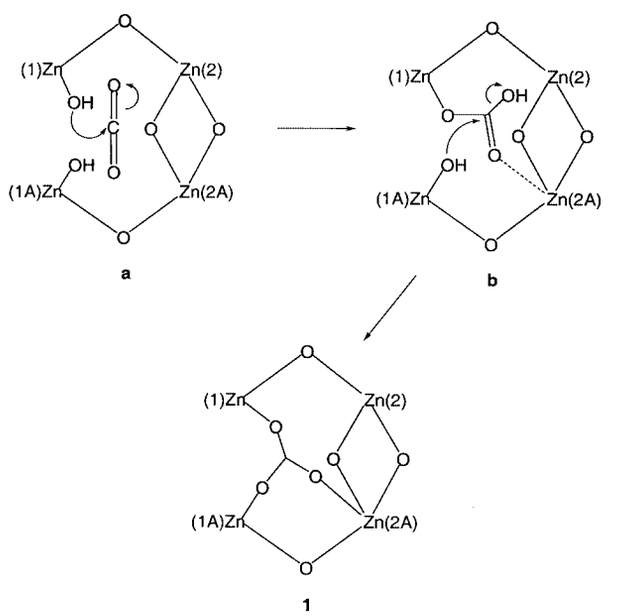


Fig. 4 Schematic representation of the cationic complex **1**.

reduced to 3.45 Å with a cresolate bridging angle [Zn(2A)–O(1A)–Zn(1A)] of 118.1° and the doubly bridged (μ_1, μ_1) Zn(2)···Zn(2A) distance is much shorter at 3.05 Å with acute bridging angles of 96.5° [Zn(2)–O(2)–Zn(2A)] and 95.6° [Zn(2)–O(2A)–Zn(2A)]. The remaining singly bridged (μ_2) Zn(1)···Zn(1A) distance is much extended at 5.63 Å due to the *anti–anti* carbonate binding mode.[17] There are five methanol and four water molecules present; three of the attending water molecules are disordered and refined to occupancies of 40.4 : 59.6 [O(5W) and O(3W)] and 68.6 : 31.4% [O(6W)]. One BF_4^- anion is disordered with two of the fluorine atoms having 58.4 : 41.6% occupancy and B(2) refined to an occupancy of 68.6 : 31.4%.

In previous structures bearing a μ_3-carbonato group the precursor has been a mononuclear complex and so no subsidiary bridging has been present in the molecular framework.[6–11] In complex **1** the precursor is the $[Zn_2L]$ unit and a possible route for the formation of **1** from this unit is given in Scheme 1. It is



Scheme 1 A suggested route for the formation of the carbonate bridge in complex **1**.

likely that in the presence of weakly or non-coordinating anions such as ClO_4^- and BF_4^- two $[Zn_2L]$ units can interact with each other through their pendant phenolato oxygen atoms to give a tetranuclear bis(μ-phenolato)bridged species. Vacant coordination sites on the terminal zinc atoms Zn(1) and Zn(1A) are then hydrated and under the basic conditions of the experiment generate coordinated hydroxides (Scheme 1: a).[6,10,16] Nucleophilic attack by the activated hydroxide at Zn(1) on carbon dioxide, from the atmosphere, would lead to the generation of

the bicarbonato species (Scheme 1: b) which could be further attacked by the hydroxide at Zn(1A) to give complex **1**. A signal assignable to the carbonate anion has been detected at δ 168.1 in the ^{13}C NMR spectrum run in d_6-DMSO.† [10]

By analogy a related complex was prepared by the reaction of H_2L with $Zn(ClO_4)_2{\cdot}6H_2O$ analysing as $[Zn_4L_2(CO_3)](ClO_4)_2{\cdot}2H_2O$, complex **2**.† Whilst no crystal structure has been obtained for this compound it is proposed that **2** is also a tetranuclear species with a similar mode of carbonate binding to that in complex **1**.

Acknowledgements

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Notes and references

† Complex **1**. H_2L (119 mg, 0.22 mmol) was dissolved in warm methanol (15 cm^3). NEt_3 (2 equivalents) and $Zn(BF_4)_2{\cdot}xH_2O$ (x = 5,6) (105 mg, 0.44 mmol) were added and the solution refluxed for 1.5 hours. The solution was cooled to rt and left to stand for three weeks during which time colourless crystals suitable for X-ray analysis grew. Yield = 47 mg (12%). Found: C, 50.1; H, 4.4; N, 8.2%. Required for $[Zn_4L_2(CO_3)](BF_4)_2{\cdot}2CH_3OH{\cdot}3H_2O$; C, 50.2; H, 4.7; N, 8.2%. ^{13}C NMR (400 MHz, d_6-DMSO): δ 168.1 (μ_3-CO_3).

Complex **2**. H_2L (108 mg, 0.2 mmol) was dissolved in warm methanol (15 cm^3). NEt_3 (2 equivalents) and $Zn(ClO_4)_2{\cdot}6H_2O$ (149 mg, 0.4 mmol) were added and the solution refluxed for 1.5 hours. The solution was cooled to rt and small colourless crystals formed; these were too small for X-ray analysis. On drying a white powder was recovered. Yield = 139 mg (42%). Found: C, 49.9; H, 4.3; N, 8.4%. Required for $[Zn_4L_2(CO_3)](ClO_4)_2{\cdot}2H_2O$; C, 50.4; H, 4.4; N, 8.5%. ^{13}C NMR (400 MHz, d_6-DMSO): δ 168.1 (μ_3-CO_3).

CAUTION! Although we have experienced no difficulties with the perchlorate salts they should nevertheless be regarded as hazardous and treated with care.

‡ Crystal data for **1**: $C_{74}H_{94}B_2F_8N_{10}O_{16}Zn_4$, M = 1814.69, monoclinic, $P2_1/c$ (C_{2h}^5, no. 14), a = 17.917(3), b = 16.457(3), c = 29.134(4) Å, α = 90, β = 104.467(3), γ = 90°, U = 8318(2) Å^3, Z = 4, μ = 1.226 mm^{-1}, T = 150(2) K, R_1 = 0.0772 (wR_2 = 0.2352, for all 19741 data, 1007 parameters). CCDC reference number 171033. See http://www.rsc.org/suppdata/dt/b1/b108432c/ for crystallographic data in CIF or other electronic format.

§ In this Communication the subscript n in the designation μ_n refers to the number of donor atoms used in the bridge.

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