DALTON
FULL PAPER

Spontaneous carbon dioxide fixation: a μ_4-carbonate bridged tetranuclear zinc(II) complex of a heptadentate Schiff base †

Matilde Fondo,[a] Ana M. García-Deibe,[a] Manuel R. Bermejo,*[a] Jesús Sanmartín[a] and Antonio L. Llamas-Saiz[b]

[a] *Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*
[b] *Unidade de Raios X. RIAIDT. Vicerrectorado de Investigación, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*

Received 23rd September 2002, Accepted 24th October 2002
First published as an Advance Article on the web 25th November 2002

The electrochemical reaction of zinc and 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine (H_3L^1) in acetonitrile in air yields the tetranuclear zinc complex $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$, which crystallises with different solvent molecules in two different systems: $[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ **1a** (monoclinic, *Pn*) and $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ **1b** (triclinic, $P\bar{1}$). The electrochemical reaction under a nitrogen stream leads to the isolation of crystals of $[(Zn_2L)_2(CO_3)]\cdot 0\cdot 25H_2O\cdot 2CH_3CN$ **1c** (monoclinic $P2_1/c$). All structures demonstrate the striking ability of this system to spontaneously fix carbon dioxide. The crystals solution reveal a μ_4-η^2:η^1:η^1 binding mode for the carbonate group in all cases, leading to a tetranuclear complex by self-assembly of dinuclear units. Chemical reaction of $Zn(CH_3COO)_2\cdot 2H_2O$ with H_3L yields $[Zn_2L(CH_3COO)]\cdot 2H_2O$. Its recrystallisation allows isolating $[Zn_2L(CH_3COO)]\cdot 2H_2O\cdot CH_3OH$ **2**. Reaction of $[Zn_2L(CH_3COO)]\cdot 2H_2O$ with $(CH_3)_4NOH\cdot 5H_2O$ leads, again, to the tetranuclear carbonate compound.

Introduction

The fixation of atmospheric carbon dioxide by metal complexes, as a way of converting this raw material in carbon-containing compounds, has been subject of special interest in the last few years.[1–9] In addition, the conversion of CO_2 to useful materials by metal complexes is also of great significance for the comprehension of the activity of some biological systems.

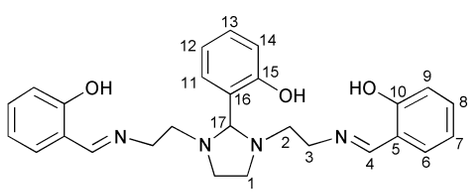
The enzyme whose function is apparently directly related to the fixation of CO_2 by hydroxo–metal complexes is carbonic anhydrase.[10] Attempts to mimic the active site of this enzyme led to the isolation of many model compounds, which allowed a significant advance in the understanding of the hydration and dehydration of bicarbonate catalysed by carbonic anhydrase.[11] Besides, these studies contributed to the knowledge of the carbonate-ligand chemistry, due to the isolation of several zinc carbonate complexes, by means of CO_2 fixation from air. Monomeric and dimeric carbonic anhydrase models have provided mono-, di- or trinuclear carbonate zinc compounds but tetranuclear carbonate bridged zinc complexes are still rare in the literature. In fact, just one tetranuclear μ_3-[12] and one μ_4-carbonate[13] zinc complexes were previously described in the literature.

In this work, a neutral tetranuclear μ_4-carbonate zinc compound, obtained by spontaneous carbon dioxide fixation from two different synthetic routes, is described.

Results and discussion

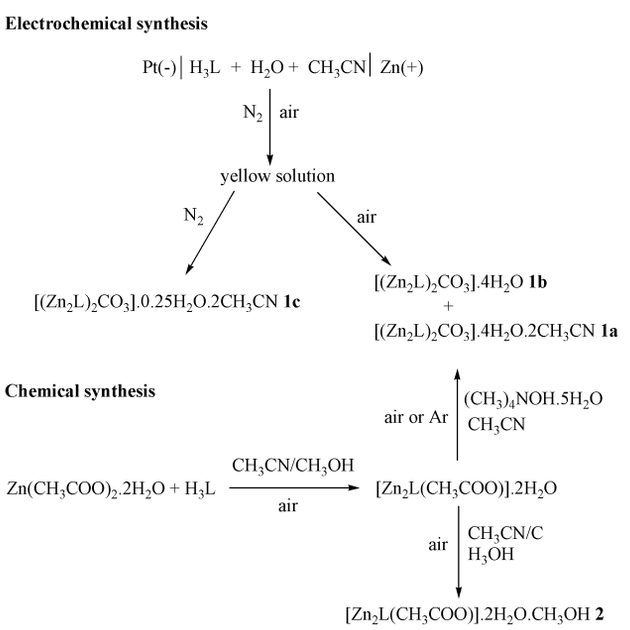
Synthesis of the metal complex

The heptadentate ligand H_3L (Scheme 1) was synthesised as previously described.[14] It was satisfactorily characterised by elemental analysis, mass spectrometry, IR and ^1H NMR spectroscopy.



Scheme 1 Schematic representation of H_3L.

Zinc complexes of H_3L were obtained by two different routes: electrochemical and chemical (Scheme 2). Reaction of an acetonitrile solution of H_3L with zinc in an electrochemical cell in air yields a yellow solution. Its slow evaporation leads



Scheme 2 Routes for the isolation of the metal complexes.

† Electronic supplementary information (ESI) available: ORTEP diagrams for **1b** and **1c**. See http://www.rsc.org/suppdata/dt/b2/b209328f/

 DOI: 10.1039/b209328f

Table 1 Selected bond lengths (Å) and angles (°) for **1a**

Zn(11)–O(11)	1.993(5)	O(13)–C(10)	1.246(10)
Zn(11)–O(101)	1.970(4)	Zn(21)–O(12)	1.965(5)
Zn(11)–O(103)	2.087(5)	Zn(21)–O(201)	2.013(5)
Zn(11)–N(101)	2.057(6)	Zn(21)–O(203)	1.985(5)
Zn(11)–N(103)	2.258(5)	Zn(21)–N(201)	2.027(6)
Zn(12)–O(11)	1.957(5)	Zn(21)–N(203)	2.312(6)
Zn(12)–O(102)	1.984(5)	Zn(22)–O(13)	1.982(5)
Zn(12)–O(103)	2.063(5)	Zn(22)–O(202)	1.998(5)
Zn(12)–N(102)	2.023(6)	Zn(22)–O(203)	1.995(5)
Zn(12)–N(104)	2.307(6)	Zn(22)–N(202)	1.992(7)
O(11)–C(10)	1.321(9)	Zn(22)–N(204)	2.298(5)
O(12)–C(10)	1.259(10)		
O(101)–Zn(11)–N(103)	170.4(2)	O(201)–Zn(21)–N(203)	157.7(2)
O(11)–Zn(11)–N(101)	131.5(2)	O(12)–Zn(21)–N(201)	101.2(2)
O(11)–Zn(11)–O(103)	80.69(19)	O(12)–Zn(21)–O(203)	108.1(2)
N(101)–Zn(11)–O(103)	144.6(2)	N(201)–Zn(21)–O(203)	149.9(2)
O(102)–Zn(12)–N(104)	167.9(2)	O(202)–Zn(22)–N(204)	166.1(2)
O(11)–Zn(12)–N(102)	128.7(2)	O(13)–Zn(22)–N(202)	108.7(2)
O(11)–Zn(12)–O(103)	82.1(2)	O(13)–Zn(22)–O(203)	109.0(2)
N(102)–Zn(12)–O(103)	144.1(2)	N(202)–Zn(22)–O(203)	141.2(2)
Zn(12)–O(103)–Zn(11)	94.4(2)	Zn(21)–O(203)–Zn(22)	107.6(2)
Zn(12)–O(11)–Zn(11)	100.9(2)		

to isolation of $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$, which crystallises as $[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ **1a** and $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ **1b**. This experiment shows that the H_3L/zinc system can fix carbon dioxide, converting it into the carbonate ligand.

The electrochemical synthesis was performed under a nitrogen stream, in an attempt to avoid air, the most probable source of CO_2. Concentration of the yellow solution so obtained gives crystals of $[(Zn_2L)_2(CO_3)]\cdot 0.25H_2O\cdot 2CH_3CN$ **1c**. Replacement of nitrogen by an argon stream, in order to avoid or reduce the CO_2 presence to the minimum, does not allow the isolation of any pure product from the reaction cell.

The interaction of zinc and H_3L was also studied by a classical chemical method. Reaction of zinc acetate with H_3L in air yields $[Zn_2L(CH_3COO)]\cdot 2H_2O$. Recrystallisation of the product in acetonitrile/methanol leads to crystals of $[Zn_2L(CH_3COO)]\cdot 2H_2O\cdot CH_3OH$ **2**, which is stable in air in the solid state and in solution. Following a related procedure,[15] $[Zn_2L(CH_3COO)]\cdot 2H_2O$ was reacted with $(CH_3)_4NOH\cdot 5H_2O$ in acetonitrile in air. The insoluble bulk pale yellow material so obtained was characterised by elemental analysis, mass spectrometry and NMR spectroscopy. The signal at *ca.* 165 ppm in the ^{13}C NMR spectrum seems to indicate that the sample is, again, the tetranuclear carbonate-complex. Recrystallisation of the bulk sample in acetonitrile in air gives complex **1a**, corroborated by X-ray diffraction studies.

The fact that the acetate complex could be isolated and was stable in air but yielded the carbonate complex in the presence of $(CH_3)_4NOH\cdot 5H_2O$, seems to indicate that fixation of carbon dioxide only proceeds in a basic medium in this case study. Therefore, it seems that the hydroxy reactant plays an important role in the reaction mechanism of carbon dioxide absorption.

Attempts to corroborate this point were made, since reaction of acetate complexes with hydroxy ligands in an inert atmosphere to yield hydroxy complexes is well documented in the literature.[13,15,16] Thus, the chemical reaction was carried out in boiled acetonitrile under an argon atmosphere. The pale yellow solid isolated shows a ^{13}C NMR spectrum typical of the tetranuclear carbonate complex. This makes evident that our hard efforts to maintain an inert atmosphere always resulted in adventitious addition of CO_2 to the complex, showing the extraordinary ability of this system to react with carbon dioxide.

X-Ray diffraction studies

Crystal structure of $[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ 1a. Single crystals of $[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ **1a**, $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ **1b** and $[(Zn_2L)_2(CO_3)]\cdot 0\cdot 25H_2O\cdot 2CH_3CN$ **1c**, suitable for X-ray diffraction studies, were grown as detailed in the Experimental section. This analysis shows that **1a**, **1b** and **1c** are essentially the same chemical compound and consists of tetranuclear neutral $[(Zn_2L)_2(\mu_4\text{-}CO_3)]$ units with acetonitrile and water as solvates. For this reason, only **1a** should be described. The ORTEP diagrams and crystallographic data for **1b** and **1c** are deposited as ESI. †

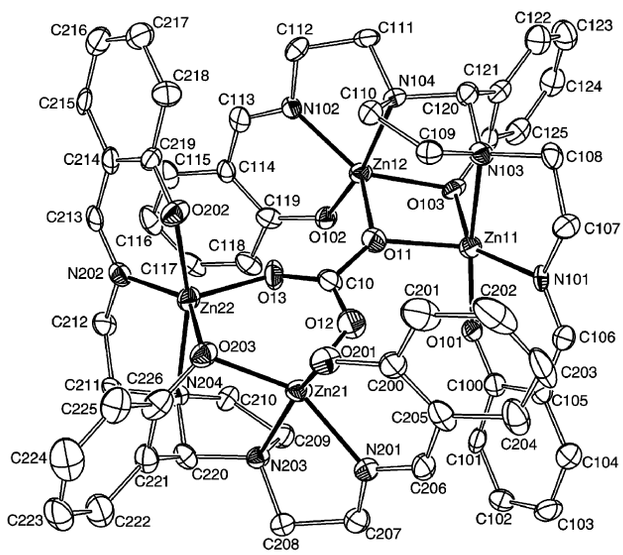


Fig. 1 An ORTEP view of the crystal structure of $[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ **1a**. Solvent molecules are omitted for clarity. Ellipsoids are drawn at 40% probability.

An ORTEP view of **1a** is shown in Fig. 1. Experimental details are given in Table 3 (see Experimental) and selected bond lengths and angles in Table 1.

The structure of the complex can be understood as two dinuclear $[Zn_2L]^+$ units bridged by the carbonate ligand. The compartimental trianionic $[L]^{3-}$ ligand has two tridentate cavities (formed by one phenol oxygen, one imine and one amine nitrogen atom), each one allocating a zinc ion. In addition, the phenol oxygen atom of the middle ligand arm bridges both metal centres. Additionally, a carbonate ligand joins two $[Zn_2L]^+$ units. Thus, the tetranuclear structure can be considered as obtained by assembly of two dinuclear components (Fig. 2).

The four zinc atoms are placed on the vertexes of a distorted rectangle (intradinuclear ZnX1 ··· ZnX2 distances of *ca.* 3 Å;

Table 2 Selected bond lengths (Å) and angles (°) for **2**

Zn(11)–O(103)	1.988(3)	Zn(12)–O(103)	1.980(3)
Zn(11)–O(11)	1.990(3)	Zn(12)–O(12)	1.989(3)
Zn(11)–O(101)	1.992(3)	Zn(12)–O(102)	1.997(3)
Zn(11)–N(101)	2.011(3)	Zn(12)–N(102)	2.008(4)
Zn(11)–N(103)	2.414(3)	Zn(12)–N(104)	2.385(3)
O(103)–Zn(11)–O(11)	108.34(13)	O(103)–Zn(12)–O(12)	109.33(13)
O(103)–Zn(11)–N(101)	136.52(12)	O(103)–Zn(12)–N(102)	139.17(14)
O(11)–Zn(11)–N(101)	113.15(14)	O(12)–Zn(12)–N(102)	109.51(15)
O(101)–Zn(11)–N(103)	163.73(14)	O(102)–Zn(12)–N(104)	162.49(13)
Zn(11)–O(103)–Zn(12)	109.32(12)		

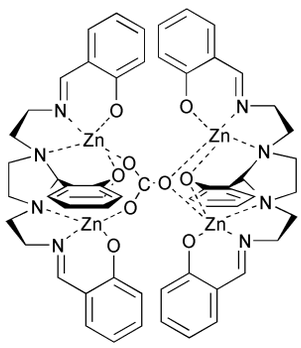


Fig. 2 Schematic representation of the $[(Zn_2L)_2(CO_3)]$ complex.

interdinuclear Zn1X ··· Zn2X distances of *ca.* 5 Å, with X = 1, 2), the shortest Zn ··· Zn distance corresponding to the zinc atoms of the Zn_2O_2 ring (distance Zn11 ··· Zn12 of 3.0451(13) Å). This distance compares fairly well with those found in dinuclear zinc complexes containing an endogenous and an exogenous O-bridge.[17]

Each zinc atom is in a pentacoordinated N_2O_3 environment (Fig. 3). Analysis of the τ parameter [*ca.* 0.4 except for Zn21

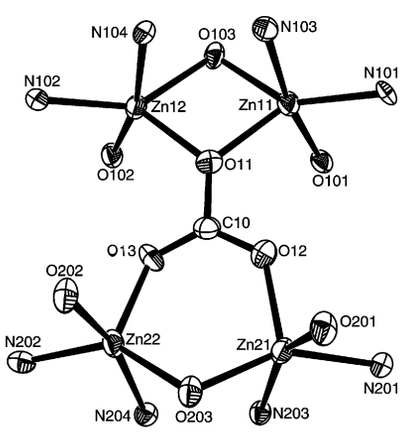


Fig. 3 The core of the tetranuclear complex.

(0.13)] indicates geometry between square pyramidal and trigonal bipyramidal for three of the four zinc atoms and a distorted square pyramidal environment for Zn21. The Zn–N and Zn–O distances are in the expected range,[18–20] with the Zn–N_{imine} distances being significantly shorter than the Zn–N_{amine} ones. The angles around the zinc atoms, which range from 78.4(2) to 170.4(2)°, clearly show the high distortion of the polyhedron.

The carbonate ligand is acting in a μ_4-η^2:η^1:η^1 fashion: one oxygen atom bridges two metal centres, giving rise to a four-membered Zn_2O_2 nearly planar ring, and the other two oxygen atoms are linked in a *syn–syn* binding mode to each one of the remaining zinc atoms and form a six-membered $Zn_2(O)CO_2$ chelate ring. The different Zn–$O_{carbonate}$ and C–$O_{carbonate}$ distances reflect the asymmetric nature of the carbonate bridge: the bridging $\mu_2\eta^2$–O atom shows the longest

Table 3 Crystal data and structure refinement for **1a** and **2**

	1a	**2**
Empirical formula	$C_{59}H_{68}N_{10}O_{13}Zn_4$	$C_{30}H_{37}N_4O_8Zn_2$
Formula weight	1386.71	712.38
Temperature/K	120.0(1)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	*Pn*	$P\bar{1}$
a/Å	11.828(2)	10.058(3)
b/Å	17.039(4)	11.470(3)
c/Å	15.706(3)	15.581(4)
α/°	90	94.238(4)
β/°	109.784(4)	93.770(4)
γ/°	90	109.993(4)
Z	2	2
Absorption coefficient/mm^{-1}	1.664	1.482
Crystal size/mm^3	0.24 × 0.20 × 0.14	0.81 × 0.28 × 0.17
Reflections collected	19198	6822
Independent reflections	9302 [*R*(int) = 0.0328]	6822
Absorption correction	SADABS	SADABS
Data/restraints/parameters	9302/2/778	6822/0/405
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0499 *wR*2 = 0.1184	*R*1 = 0.0468 *wR*2 = 0.1482
R indices (all data)	*R*1 = 0.0668 *wR*2 = 0.1320	*R*1 = 0.0659 *wR*2 = 0.1631

C–O distance, as expected.[13,21–23] Besides, the Zn–$\mu_2\eta^2$–$O_{carbonate}$ distances are significantly different for the same $[Zn_2L]^+$ unit, showing the asymmetry of the Zn–$O_{carbonate}$–Zn bridge. This also occurs with the Zn–μ_2-O_{phenol} distances, that clearly shows the non-symmetric nature of the Zn–O_{phenol}–Zn bridge.

Complex **1a** contains four water molecules in the unit cell that give rise to intramolecular hydrogen bonds. For each $[Zn_2L]^+$ unit, one water molecule interacts with both phenol oxygen atoms [distances O(1W) ··· O(101), O(1W) ··· O(102), O(3W) ··· O(201) and O(3W) ··· O(202) ranging from 2.750(8) to 2.878(8) Å]. The second water molecule per dinuclear unit is hydrogen bonded to the first one [distances O(1W) ··· O(2W) 2.719(9) Å and O(3W) ··· O(4W) 2.725(9) Å]. These interactions contribute to ensure the cohesion of the crystal lattice, which is highly ordered.

Crystal structure of $[Zn_2L(CH_3COO)]\cdot 2H_2O\cdot CH_3OH$ 2. An ORTEP view of **2** is shown in Fig. 4. Experimental details are given in Table 3 and selected bond lengths and angles in Table 2.

Complex **2** consists of dinuclear neutral $Zn_2L(CH_3COO)$ units with methanol and water as solvates. Each zinc atom is in an N_2O_3 environment, made up of one amine nitrogen, one imine nitrogen and one terminal phenol oxygen atom. Besides, the metal atoms are doubly bridged by an endogenous phenol oxygen atom of the central ligand arm and by an exogenous acetate group, acting as bridging bidentate in a *syn–syn* mode. The coordination geometry can be considered as intermediate between square pyramidal and trigonal bipyramidal, as it is

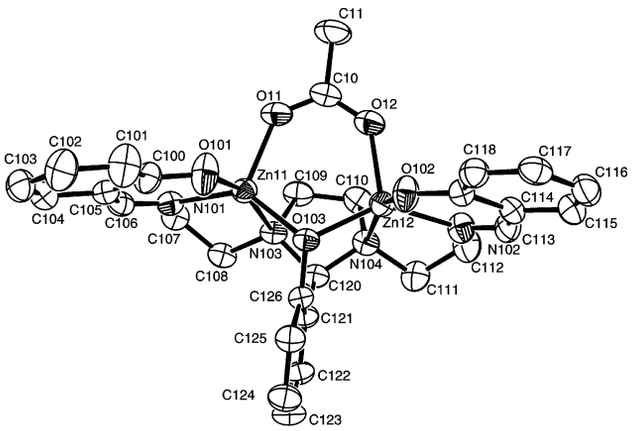


Fig. 4 An ORTEP view of $[Zn_2L(CH_3COO)]\cdot 2H_2O\cdot CH_3OH$ **2**. Solvent molecules are omitted for clarity. Ellipsoids are drawn at 40% of probability.

reflected by the index of trigonality τ (*ca.* 0.45 for Zn11 and 0.4 for Zn12).

The Zn–N and Zn–O distances are in the expected range.[13,17,18] The Zn–O distances for the bridging phenoxy interactions indicate that this bridge is practically symmetric [Zn(11)–O(103) 1.988(3) Å; Zn(12)–O(103) 1.980(3) Å]. Similarly, the Zn(11)–O(11) and Zn(12)–O(12) distances [Zn(11)–O(11) 1.990(3) Å; Zn(12)–O(12) 1.989(3) Å] show a high degree of symmetry for the acetate bridge. The intermetallic separation is *ca.* 3.24 Å and compares fairly well with metal distances found for similar complexes.[15,24]

The angles around zinc atoms, ranging from 78.85(13) to 163.73(14) show a high distortion from the ideal geometry.

Complex **2** shows an intricate hydrogen bond scheme among solvate molecules and the phenol and acetate oxygen atoms. Two water molecules [O(2w) and O(3w)] are at 50% occupancy, with O(3w) disordered over two sites. Thus, one water molecule (O1w) gives rise to intramolecular interactions with both terminal phenol oxygen atoms [O(1W) ··· O(101) 2.935(5) Å; O(1W) ··· O(102) 2.827(5) Å] and with the methanol molecule [O(1S) ··· O(1W) 2.746(8) Å]. The methanol solvent also interacts with O(3w) [O(1S) ··· O(3W) 2.734(18) Å]. O(2w) shows a short intramolecular interaction with an acetate oxygen atom [O(2W) ··· O(12) 2.932(9) Å] and two long intermolecular hydrogen bonds with one terminal phenol and one acetate oxygen atom of a neighbouring unit [O(2W) ··· O(101)* 3.210(10) Å; O(2W) ··· O(11)* 3.269(11) Å]. In addition, a water molecule of a neighbouring unit [O(2W*)] interacts with O(101) and O(11). This give rise to a disposition of the molecules in the unit cell as shown in Fig. 5, that resembles a tetranuclear dimer made up of two weakly joined dinuclear monomers.

Spectral characterisation

The IR, mass, ^{1}H and ^{13}C NMR spectra of $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ and $[Zn_2L(CH_3COO)]\cdot 2H_2O$ (see Experimental section) are consistent with their expected structures and with stability of the complexes in solution.[25–28]

The ^{1}H NMR spectra of both complexes show two sets of aromatic signals, arising from the non-equivalent terminal and central ligand arms. This result also states that there is only one species and that both $[Zn_2L]^+$ units of the carbonate complex are equivalent in solution. A singlet at 1.99 ppm (3 H) for $[Zn_2L(CH_3COO)]\cdot 2H_2O$ agrees with the coordination of the acetate group to the metal centres in solution.

In addition, the ^{13}C NMR spectrum of $[Zn_2L(CH_3COO)]\cdot 2H_2O$ shows peaks typical of coordinated acetate (163.27 and 23.55 ppm). The spectrum of the carbonate complex shows a new peak at 165.11 ppm, assigned to the carbonate group. This signal is in the range of those found for carbonate-bridged complexes.[12,29–31]

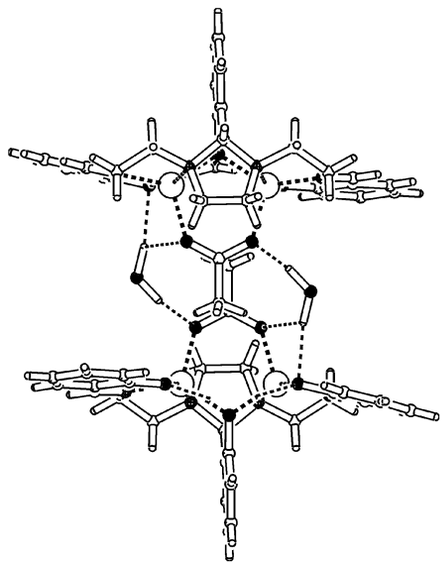


Fig. 5 A view of the disposition of two neighbouring molecules in complex **2**, showing the weakly joined dinuclear units.

Finally, it should be noted that both ^{13}C and ^{1}H NMR spectra of the complex obtained by chemical reaction between $[Zn_2L(CH_3COO)]\cdot 2H_2O$ and $(CH_3)_4NOH\cdot 5H_2O$, clearly indicates that the acetate ligand was replaced by a carbonate ligand.

As a result of the studies performed and the characterisation techniques employed, it can be concluded that the zinc/H_3L system in an electrochemical cell readily absorbs carbon dioxide to generate a tetranuclear zinc carbonate compound in a unique step. The chemical reaction of zinc acetate with H_3L in air allows isolation of $[Zn_2L(CH_3COO)]\cdot 2H_2O$, that can not survive in solution in the presence of $(CH_3)_4NOH$, yielding, again, the carbonate complex. Attempts to maintain an inert atmosphere always resulted in addition of CO_2 to the complex, preventing the isolation of any intermediate and evidencing the extremely high reactivity of this system towards carbon dioxide.

Experimental

Chemicals

All solvents, salicyladehyde, triethylenetetramine, tetramethylamonium hydroxide pentahydrate and zinc acetate dihydrate are commercially available and were used without further purification. Zinc (Ega Chemie) was used as *ca.* 2 × 2 cm^2 plates.

Physical measurements

Elemental analyses of C, H and N were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on a Bruker AC-300 spectrometer using DMSO-d_6 as solvent. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. Electrospray mass spectra were obtained on a Hewlett-Packard LC/MS spectrometer, in methanol as solvent.

Synthesis of the ligand and metal complexes

H_3L was prepared following a related procedure[14] and fully characterised by elemental analysis, mass spectrometry, IR and ^{1}H NMR spectroscopy. Anal. Calc. for H_3L ($C_{27}H_{30}N_4O_3$): C, 70.7; H, 6.5; N, 12.2. Found: C, 70.2; H, 6.7; N, 12.4%. MS(ES): *m*/*z* 459 (H_4L^+). IR (KBr, ν/cm^{-1}): 1632 (C=N), 3434 (OH). ^{1}H NMR (300 MHz, DMSO-d_6): 2.64 (q, 2H, H^{2ax}), 2.70 (q, 2H, H^{1ax}), 2.84 (q, H^{2eq}), 3.35 (m, H1eq), 3.60 (t, 4H, H^3), 4.02

(s, 1H, H^{17}), 6.65 (d, 1H, H^{14}), 6.73 (dd, 1H, H^{12}), 6.89–6.83 (m, 4H, H^7 + H^9), 7.15 (m, 2H, H^{11} + H^{13}), 7.31 (dd, 2H, H^8), 7.36 (d, 2H, H^6), 8.43 (s, 2H, H^4), 10.86 (br, 1H, OH), 13.77 (br, 2H, OH).

$[(Zn_2L)_2(CO_3)]\cdot 4H_2O$: an acetonitrile solution of H_3L (0.1 g, 0.218 mmol), containing *ca.* 10 mg of tetramethylammonium perchlorate, was electrolysed at 10 mA, for 2 h 20 min, using a platinum wire as cathode and a zinc plate as anode. Slow evaporation of the resultant yellow solution yielded crystals of $[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ **1a** and $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ **1b**, suitable for X-ray diffraction studies. The analysis of the bulk sample is in agreement with the $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ proposed stoichiometry. Calc. for $[(Zn_2L)_2(CO_3)]\cdot 4H_2O$ ($C_{55}H_{62}N_8O_{13}Zn_4$): C, 50.6; H, 4.8;N, 8.6. Found: C, 50.5; H, 4.7; N, 8.7%. MS(ES): *m*/*z* 585 $[Zn_2L]^+$, 629 $[Zn_2L(CO_2)]^+$, 647 $[Zn_2L(CO_3)_2H]^+$, 1217 $[(Zn_2L)_2(CO_2)]^+$, 1231 $[(Zn_2L)_2(CO_3)H]^+$. IR (KBr, ν/cm^{-1}): 1535, 1347 (CO_3), 1633 (C=N), 3434 (OH). NMR (300 MHz, DMSO-d_6): ^{1}H NMR: 2.71–2.56 (m, 6H, H^{1ax} + H^{2ax} + $2H^3$), 3.23 (m, 2H, H^{2eq}), 3.63 (t, 2H, $2H^3$), 3.83 (m, 2H, H^{1eq}), 3.99 (s, 1H, H^{17}), 6.41 (dd, 2H, H^7), 6.56–6.66 (m, 4H, $2H^9$ + H^{12} + H^{14}), 7.02–7.10 (m, 4H, $2H^6$ + H^{11} + H^{13}), 7.19 (dd, 2H, H^8), 8.31 (s, 2H, H^4). ^{13}C NMR: 49.96 (C^2), 52.34 (C^3), 53.86 (C^1), 89.88 (C^{17}), 117.96, 116.50 (C^5 + C^{16}), 130.76 (C^{10}), 135.35, 133.65, 132.21, 122.31, 122.05, 121.26, 112.32 (C^6–C^9 + C^{11}–C^{14}), 165.11 (CO_3), 170.84 (C^4), 171.24 (C^{15}).

The same complex was obtained when an acetonitrile solution of $Zn_2L(CH_3COO)\cdot 2H_2O$ was treated with tetramethylamonium hydroxide pentahydrate in air and/or under an argon (99.999%) stream.

$[(Zn_2L)_2(CO_3)]\cdot 0.25H_2O\cdot 2CH_3CN$ **1c**: through an acetonitrile (80 mL) solution of H_3L (0.1 g, 0.218 mmol), containing *ca.* 10 mg of tetramethylammonium perchlorate, a nitrogen stream was passed for 1 h. Then, the solution was electrolysed under a nitrogen stream at 10 mA, for 2 h 20 min, using a platinum wire as cathode and a zinc plate as anode. The resultant yellow solution was concentrated and after reduction of its volume to ½, small yellow crystals of **1c**, suitable for X-ray diffraction studies, were isolated.

$[Zn_2L(CH_3COO)]\cdot 2H_2O$: To a methanol (20 mL) solution of $Zn(CH_3COO)\cdot 2H_2O$ (0.25 g, 1.14 mmol), an acetonitrile (20 mL) solution of H_3L (0.26 g, 0.57 mmol) was added. The resultant yellow solution was stirred in air for 4 h. and a pale yellow solid precipitated. The solid was filtered and washed with diethylether. Recrystallisation in methanol/acetonitrile yields crystals of $[Zn_2L(CH_3COO)]\cdot 2H_2O\cdot CH_3OH$ **2**, suitable for X-ray diffraction studies. Calc. for $Zn_2L(CH_3COO)\cdot 2H_2O$ ($C_{29}H_{33}N_4O_5Zn_2$): C, 51.1; H, 5.0;N, 8.2. Found: C, 50.7; H, 5.0; N, 8.0%. MS(ES): *m*/*z* 585 $[Zn_2L]^+$, 645 $[Zn_2L(CH_3COOH)]^+$. IR (KBr, ν/cm^{-1}): 1574, 1450 (COO), 1630 (C=N), 3447 (OH). NMR (300 MHz, DMSO-d_6): ^{1}H NMR: 1.99 (s, 3H, CH_3), 2.62 (m, 2H, $2H^{3ax}$), 2.72–2.80 (m, 4H, H^{1ax} + H^{2ax}), 3.36 (m, 2H, H^{2eq}), 3.62 (m, 2H, $2H^{1eq}$), 3.75 (m, 2H, $2H^{3eq}$), 4.12 (s, 1H, H^{17}), 6.40 (dd, 2H, H^7), 6.72–6.79 (m, 6H, $2H^8$ + $2H^9$ + H^{12} + H^{14}), 7.04–7.18 (m, 4H, $2H^6$ + H^{11} + H^{13}), 8.32 (s, 2H, H^4). ^{13}C NMR: 23.55 (CH_3), 50.25 (C^2), 53.97 (C^3), 54.29 (C^1), 89.51 (C^{17}), 117.59, 118.92 (C^5 + C^{16}), 131.03 (C^{10}), 132.36, 133.83, 135.24, 123.52, 122.18, 121.47, 112.38 (C^6–C^9 + C^{11}–C^{14}), 163.27 (COO), 171.01 (C^4), 171.66 (C^{15}).

Crystallographic measurements

Crystal data and details of refinement are given in Table 3.

$[(Zn_2L)_2(CO_3)]\cdot 4H_2O\cdot 2CH_3CN$ 1a and $[Zn_2L(CH_3COO)]\cdot 2H_2O\cdot CH_3OH$ 2. Crystals of **1a** and **2**, suitable for single-crystal X-ray studies, were obtained as previously described. Data were collected at 120 K for **1a** and 293 K for **2** on a Bruker SMART 1000 diffractometer, employing graphite-monochromated Mo–Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full matrix least squares based on F^2.[32] An SADABS absorption correction was applied. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms bonded to carbon were included in the structure factor calculation in idealised positions but not refined. Hydrogen attached to oxygen atoms were located in the Fourier map or not included.

CCDC reference numbers 189066 and 178741.

See http://www.rsc.org/suppdata/dt/b2/b209328f/ for crystallographic data in CIF or other electronic format.

References

1 A. Behr, *Carbon dioxide activation by metal complexes*, VCH, New York, 1988.
2 D. J. Darensboug and M. Holtcamp, *Coord. Chem. Rev.*, 1996, **152**, 155.
3 W. Leitner, *Coord. Chem. Rev.*, 1996, **153**, 257.
4 D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063.
5 X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
6 D. Walter, M. R. Ruben and S. Rau, *Coord. Chem. Rev.*, 1999, **182**, 67.
7 R. H. Bode, W. L. Driessen, F. B. Hulsberg, J. Reedijk and A. L. Spek, *Eur. J. Inorg. Chem.*, 1999, 505.
8 M. Kunert, M. Bräuer, O. Klobes, H. Görls, E. Dinjus and E. Anders, *Eur. J. Inorg. Chem.*, 2000, 1803.
9 M. Minato, D.-Y. Zhou, K.-I. Sumiura, R. Hirabayashi, Y. Yamaguchi and T. Ito, *Chem. Commun.*, 2001, 2654.
10 I. Bertini, *Struct. Bonding (Berlin)*, 1982, **48**, 45.
11 E. Kimura, *Acc. Chem. Res.*, 2001, **34**, 171 and references therein.
12 H. Adams, D. Bradshaw and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 2001, 3407.
13 M. Döring, M. Ciesielski, O. Walter and H. Görls, *Eur. J. Inorg. Chem.*, 2002, 1615.
14 L-W. Yang, S. Liu, E. Wong, S.J. Rettig and C. Orvig, *Inorg. Chem.*, 1995, **34**, 2164.
15 R. A. Allred, A. M. Arif and L. M. Berreau, *J. Chem. Soc., Dalton Trans.*, 2002, 300.
16 C. Fernandes, A. Neves, A. J. Bortoluzzi, B. Szpoganicz and E. Schwingel, *Inorg. Chem. Commun.*, 2001, **4**, 354.
17 (*a*) H. Adams, D. Bradshaw and D. E. Fenton, *Eur. J. Inorg. Chem.*, 2002, 535; (*b*) H. Adams, D. Bradshaw and D. E. Fenton, *Inorg. Chem. Commun.*, 2002, **5**, 12.
18 A. Sousa, M. R. Bermejo, M. Fondo, A. García-Deibe, A. Sousa-Pedrares and O. Piro, *New J. Chem.*, 2001, **25**, 647.
19 N. A. Bailey, E. D. McKenzie and J. M. Worthington, *Inorg. Chim. Acta*, 1977, **25**, L137.
20 U. Mukhopadhyay, L. Govindasamy, K. Ravikumar, D. Velmurugan and D. Ray, *Inorg. Chem. Commun.*, 1998, **1**, 152.
21 F. W. B. Einstein and A. C. Willis, *Inorg. Chem.*, 1981, **20**, 609.
22 A. Escuer, E. Peñalba, R. Vicente, X. Solans and M. J. Font-Badía, *J. Chem. Soc., Dalton Trans.*, 1997, 2315.
23 D. Armentano, G. De Munno, F. Lloret and M. Julve, *Inorg. Chem.*, 1999, **38**, 3744.
24 H. Adams, D. Bradshaw and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 2002, 925.
25 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **23**, 227.
26 A. L. van der Brenk, K. A. Byriel, D. P. Fairlie, L. R. Gahan, G. R. Hanson, C. J. Hawkins, A. Jones, C. H. L. Kennard, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1994, **33**, 3549.
27 U. N. Andersen, C. J. McKenzie and G. Bojosen, *Inorg. Chem.*, 1995, **34**, 1435.
28 D. F. Evans and D. A. Jakubovic, *J. Chem. Soc., Dalton Trans.*, 1988, 2927.
29 N. Kitajima, S. Hikichi, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1993, **115**, 5496.
30 (*a*) A. Schrodt, A. Neubrand and R. van Eldick, *Inorg. Chem.*, 1997, **36**, 4579; (*b*) Z.-W. Mao, F. W. Heinemann, G. Liehr and R. van Eldick, *J. Chem. Soc., Dalton Trans.*, 2001, 3652.
31 M. J. Manos, A. D. Keremidas, J. D. Woollins, A. M. Z. Slawin and T. A. Kabanos, *J. Chem. Soc., Dalton Trans.*, 2001, 3419.
32 G. M. Sheldrick, SHELX97 Programs for Crystal Structure Analysis, Institüt für Anorganische Chemie der Universität, Göttingen, Germany, 1998.