

# Rare $M_7O_2$ double tetrahedral core in molecular species: preparation, structure and properties of $[Zn_7O_2(O_2CMe)_{10}(1-Meim)_2]$ (1-Meim = 1-methylimidazole)

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The 2 : 1 reaction between  $Zn(O_2CMe)_2 \cdot 2H_2O$  and 1-Meim in refluxing MeCN gives  $[Zn_7O_2(O_2CMe)_{10}(1-Meim)_2]$  **1** which comprises two vertex-sharing tetranuclear  $Zn_4(\mu_4-O)(\eta^1:\eta^1:\mu_2-O_2CMe)_5(1-Meim)$  units; solid-state  $^{13}C$  and  $^{15}N$  NMR spectra reveal structural details of the complex.

We have recently become interested in the synthesis of mono- and di-/tri-nuclear zinc complexes containing carboxylate and imidazole ligands which would be satisfactory models for the carboxylate-histidine-metal triad catalytic centres in hydrolytic zinc enzymes.<sup>1-4</sup> This area of Zn chemistry has been poorly explored. Two groups have reported<sup>5,6</sup> the preparation and X-ray structures of the mononuclear, four-coordinate complexes  $[Zn(O_2CR)_2L_2]$ , where R = Me, Et and L = imidazole, 2-ethylimidazole.

For the better investigation of the  $Zn^{II}-RCO_2^- -L$  systems (L = various monodentate imidazoles), we have systematically varied the nature of R, L and solvent, and both the  $Zn^{II}:L$  and  $Zn^{II}:RCO_2^-$  ratios. We have found all these parameters to have an important effect on the chemical and structural identity of obtained products. We herein report that the 2 : 1 and 3.5 : 1 reactions of  $Zn(O_2CMe)_2 \cdot 2H_2O$  with 1-methylimidazole (1-Meim) in MeCN lead to the assembly of the remarkable high-nuclearity product  $[Zn_7O_2(O_2CMe)_{10}(1-Meim)_2]$  **1**.

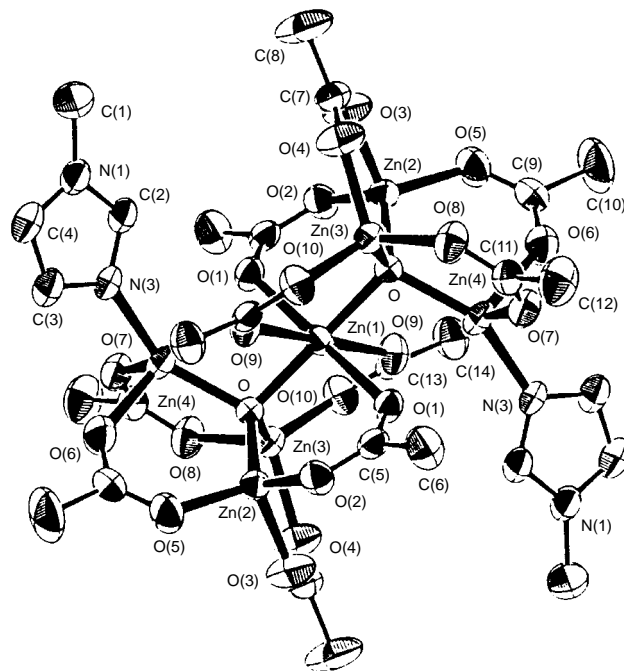
$Zn(O_2CMe)_2 \cdot 2H_2O$  (4.0 mmol) and 1-Meim (2.0 mmol) were refluxed for 30 min in MeCN (30 ml) to form a colourless solution. Layering this solution with an equal volume of  $Et_2O$  afforded colourless crystals of  $[Zn_7O_2(O_2CMe)_{10}(1-Meim)_2] \cdot 2MeCN$ , **1**·2MeCN in typical yields of ca. 45%; the dried solid analysed as **1**· $\frac{1}{2}$ . Employing a  $Zn^{II}:1-Meim$  ratio of 3.5 : 1 in either MeCN or MeOH complex **1** again results. The same procedure in EtOH can be employed for the 1,2-dimethylimidazole (1,2-diMeim) analogue of **1** ( $[Zn_7O_2(O_2CMe)_{10}(1,2-diMeim)_2]$  **2**).§

The structure of **1** (Fig. 1) is extremely unusual and consists of a  $[Zn_7(\mu_4-O)_2]^{10+}$  core. The central Zn site [Zn(1)] lies on a crystallographic inversion centre and is the shared vertex of two  $Zn_4(\mu_4-O)$  units; this unit is well established in Zn chemistry.<sup>7</sup> The peripheral ligation is provided by ten  $\eta^1:\eta^1:\mu_2$ -acetate groups and two 1-Meim ligands bonded to Zn(4) atoms; each of the five crystallographically independent acetates spans one edge of the  $Zn_4$  tetrahedron. The  $Zn_4O$  tetrahedron is slightly irregular, the Zn...Zn distances being between 3.081(1) and 3.199(1) Å and the Zn-O-Zn angles varying from 103.5 to 112.5(1)°. The shortest Zn...Zn distance between the tetrahedral subunits is the Zn(2)...Zn(4) one [5.333(1) Å]. The geometry at the central Zn is distorted octahedral, while that at the peripheral metal ions can be described as distorted tetrahedral with the distortion at Zn(4) being more severe. Bond distances to Zn(1) are distinctly longer [1.979(2)–2.203(2) Å] as expected for a higher coordination number. There appear to be stacking interactions between the centrosymmetrically parallel 1-Meim

ligands that belong to neighbouring heptanuclear molecules [closest interatomic separation,  $N(1)\cdots C(3') = C(3)\cdots N(1')$ , between opposite ligands is 3.340(5) Å]; these interactions create a form of 'chains' along the *b* axis and aid in stabilizing the crystal structure.

Complex **1** joins a small family of discrete heptanuclear zinc(II) clusters,<sup>8-11</sup> the first reported example being  $[Zn_7Me_6(OMe)_8]$ .<sup>8</sup> Complex **1** becomes the second member of a homometallic molecular complex containing the  $[M_7(\mu_4-O)_2]$  double tetrahedral unit, the only other known example<sup>10</sup> being also a zinc(II) cluster.

The compound is practically insoluble in all organic solvents; its high-resolution solid-state  $^{13}C$  NMR spectrum (recorded<sup>12</sup> at 75.5 MHz) indicates a 2 : 1 : 1 : 1 splitting of the carboxylate carbons<sup>13,14</sup> ( $\delta$  181.4–179.4) and 1 : 2 : 1 : 1 splitting of the methyl carbons ( $\delta$  24.2–22.2). Evidently, polynuclear zinc(II) complexes are excellent candidates for a comparative study of X-ray structure with solid-state NMR properties because of the



**Fig. 1** ORTEP representation of  $[Zn_7O_2(O_2CMe)_{10}(1-Meim)_2]$  **1**. Some symmetry equivalent atoms are not labelled. Selected interatomic distance ranges (Å): Zn–O(oxo) 1.914(2)–1.979(2), Zn–O(acetate) 1.944(3)–2.203(2), Zn(4)–N(3) 2.004(3), Zn...Zn 3.081–6.375(1). Selected bond angle ranges (°): *trans* at Zn(1), 180.0; *cis* at Zn(1), 81.3(1)–98.7(1); around Zn(2), 102.4(1)–120.6(1); around Zn(3), 101.5(1)–120.4(1); around Zn(4), 93.0(1)–146.2(1); Zn–O(oxo)–Zn 103.5(1)–112.5(1).

very high quality  $^{13}\text{C}$  CP MAS spectra produced and the fact that shieldings of both  $\text{CO}_2^-$  and acetate  $\text{CH}_3$  groups are very sensitive to the precise crystallographic environment. In the present complex, two of the five crystallographically inequivalent acetate ligands present in the unit cell have degenerate  $^{13}\text{C}$  chemical shifts for both methyl and carboxylate groups. The solid-state  $^{15}\text{N}$  CP MAS NMR spectrum of complex **1** indicates the presence of two resonances at  $\delta -163.6$  [N(3)] and  $\delta -212.7$  [N(1)] for the bound 1-Meim. Both resonances are significantly shifted to those of the free ligand ( $\delta -120.3$  [N(3)] and  $\delta -219.9$  [N(1)], neat liquid at 300 K, relative to  $\text{CH}_3\text{NO}_2$  as reference).

From a synthetic inorganic viewpoint, the preparation of **1** and **2** shows that it is possible to generate polynuclear zinc carboxylate complexes with unusual structures and nuclearities significantly greater than those known to date by relatively minor perturbations to the  $\text{Zn}^{\text{II}}-\text{RCO}_2^--\text{L}$  system, in this case, the use of a high  $\text{Zn}^{\text{II}}$  to L ratio. We are currently investigating the reactivity chemistry of **1** and **2** and seeking access to additional structural types.

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## Notes and References

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‡ The vacuum-dried complex analysed satisfactorily (C, H, N) as **1**.

§ Complex **2** has been characterised by single-crystal X-ray crystallography and microanalyses.

¶ *Crystal data* for **1**·2MeCN:  $\text{C}_{32}\text{H}_{48}\text{Zn}_7\text{O}_{22}\text{N}_6$ ,  $M_r = 1326.36$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.771(1)$ ,  $b = 12.616(2)$ ,  $c = 10.384(1)$  Å,  $\alpha = 107.36(1)$ ,  $\beta = 93.39(1)$ ,  $\gamma = 117.03(1)^\circ$ ,  $U = 1276.2(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 298$  K,  $\mu(\text{Cu}-\text{K}\alpha) = 4.283$  mm<sup>-1</sup>,  $D_c = 1.726$  g cm<sup>-3</sup>,  $2\theta_{\text{max}} = 143^\circ$ ,  $wR2$  (on  $F^2$ ) = 0.1044,  $R1$  (on  $F$ ) = 0.0372 for 4289 unique reflections with  $I > 2\sigma(I)$ . The number of refined parameters is 360. The structure was solved by direct methods using SHELXS-86<sup>15</sup> and refined by full-matrix

least-squares techniques using SHELXL-93.<sup>16</sup> All hydrogen atoms were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically. CCDC 182/890.

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