

A New Tetranucleating Tetra-amino-tetra-phenolic Macrocyclic Ligand and the Crystal Structure of a Zn₄ Derivative

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The macrocyclic tetra-amino-tetra-phenolate ligand L⁴⁻, from **2**, obtained by borohydride reduction of the corresponding tetra-Schiff's base macrocycle **1**, gives a tetra-zinc derivative, [LZn₄(OH)(MeCO₂)₃(MeOH)]·1.5MeOH, whose X-ray crystal structure is described.

Reasons have been presented elsewhere¹ for the realistic expectation that complexes of ligands which bind groups of metal centres in some predetermined way may show extraordinary reactivity, stemming from the organisation built into the complex. Some examples of complexes of macrocyclic ligands which bind either groups of four metal centres in a roughly planar, square or rhomboid fashion,^{1,2} or groups of six metal centres³ have been reported. These systems were assembled by Schiff's base condensation of diamine and dialdehyde building blocks and for future reactivity studies

they may suffer from the possible deficiency of undesirable reaction at the CH=N links, *e.g.* hydrolytic disruption of the macrocycle. The corresponding poly-amino ligands in which the CH=N links have been replaced by CH₂-NH promise to be chemically more robust making possible reactivity studies under more forcing conditions. In addition the poly-amino ligands would be expected to be more flexible than the corresponding poly-imines and this may be a desirable feature of a polynuclear metal derivative which is intended to promote or catalyse some sort of multi-step reaction of substrates. We

report here the first example of a potentially robust tetra-amino-tetra-phenolic macrocycle and the crystal structure of a Zn_4 derivative.

The macrocyclic tetra-Schiff's base-dihydrochloride derivative **1**[†] was reduced by excess of sodium borohydride in ethanol at 0 °C to the corresponding tetra-amino macrocycle **2** (hereafter LH_4), which was most conveniently isolated, stored and used for the synthesis of complexes in the form of its tetrahydrochloride, LH_8Cl_4 .

Solutions in methanol of LH_8Cl_4 , zinc acetate dihydrate, lithium acetate and tetra-ethylammonium hydroxide in 1 : 5 : 10 : 8 proportions after concentration by evaporation and after being allowed to cool to room temperature gave colourless crystals of solvated $LZn_4(OH)(MeCO_2)_3$ [‡] from which a specimen was selected for X-ray crystallographic analysis.^{‡4,5} One view of the structure of the complex and selected structural data are presented in Fig. 1.

The composition and overall arrangement have much in common with those of a Zn_4 derivative of the tetra-Schiff's base macrocycle **1**.[†] The four Zn centres, although not coplanar, are seen, in projection, approximately at the corners of a rhombus [long 'diagonal' $Zn(1)\cdots Zn(3)$, 5.111(2) Å; short 'diagonal' $Zn(2)\cdots Zn(4)$, 3.468(1) Å; dihedral angle between the plane passing through $Zn(1)$, $Zn(2)$ and $Zn(4)$ and that through $Zn(3)$, $Zn(2)$ and $Zn(4)$ is 39.3°]. The hydroxide is approximately centrally placed, being bonded strongly to $Zn(2)$ and $Zn(4)$ [2.029(3) and 2.012(5) Å respectively], less strongly to $Zn(3)$ [2.267(5) Å] and weakly to $Zn(1)$ [2.849(5) Å]. One acetate unit bridges $Zn(2)$ and $Zn(4)$. The two other acetates are each monodentate, one to $Zn(3)$ and the other to $Zn(1)$. A coordinated methanol molecule completes an approximately octahedral arrangement around $Zn(2)$ whilst $Zn(3)$ and $Zn(4)$ are five-coordinate and $Zn(1)$ is essentially four-coordinate with a weakly associated fifth ligand (the central OH).

The ligand arrangement is completely lacking in symmetry. All four aromatic nuclei are inclined on the same side of the Zn_4 cluster in an approximate dish or dome conformation. The relative orientations of the four NH bonds ('up' or 'down,' say) in principle could lead to a number of isomeric complexes (all up; up,up,down,down; up,down,up,down; three up, one down). The hydrogen atoms attached to the

nitrogens located by the X-ray study reveal the alternating up, down, up, down arrangement.

The ¹H and ¹³C NMR spectra of $LZn_4(OH)(MeCO_2)_3\cdot 2.5H_2O$ in $CDCl_3$ suggest that the solution species

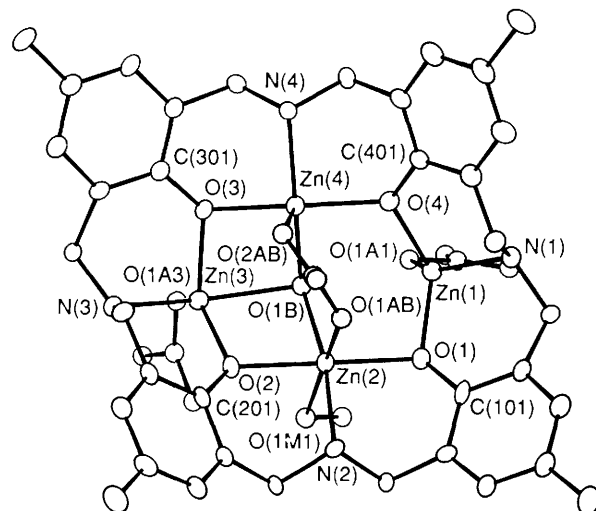
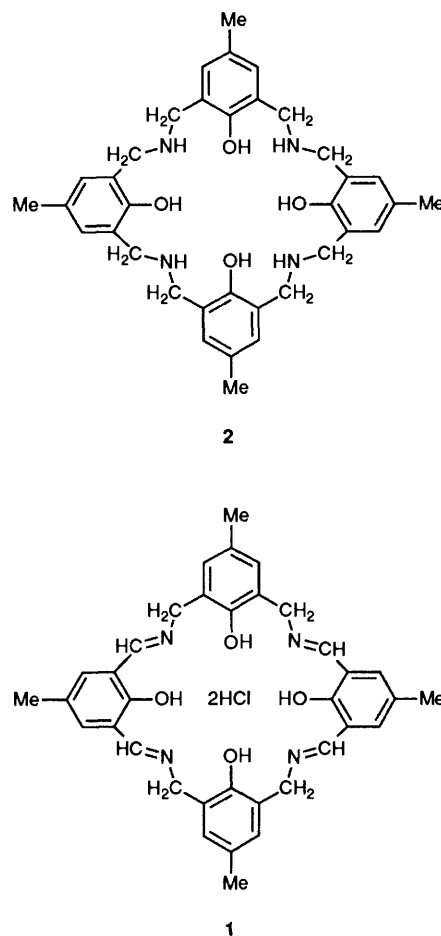


Fig. 1 ORTEP of the $[LZn_4(OH)(MeCO_2)_3(MeOH)]$ molecule. Metal to metal distances (Å) are: $Zn(1)\cdots Zn(2)$ 3.193(1), $Zn(1)\cdots Zn(3)$ 5.111(2), $Zn(1)\cdots Zn(4)$ 3.408(2), $Zn(2)\cdots Zn(3)$ 3.198(2), $Zn(2)\cdots Zn(4)$ 3.468(1), $Zn(3)\cdots Zn(4)$ 3.076(2). Ranges of Zn to donor atom distances (Å) are: Zn–O(phenolate) 1.978(3) to 2.117(5); Zn–O(hydroxide) 2.012(5) to 2.849(5); Zn–N 2.017(8) to 2.103(6).

[†] The product after being dried *in vacuo* at 80 °C and exposed to the atmosphere showed elemental analysis consistent with $LZn_4(OH)(CH_3CO_2)_3\cdot 2.5H_2O$. X-Ray crystallography revealed that the composition of the initially formed crystals was $[LZn_4(OH)(CH_3CO_2)_3(CH_3OH)]\cdot 1.5CH_3OH$.

[‡] *Crystal data*: $C_{44}H_{60}O_{13}N_4Zn_4$, $M = 1128$, monoclinic, space group $C2/c$, $a = 34.213(9)$, $b = 16.028(3)$, $c = 20.640(3)$ Å, $\beta = 119.17(2)^\circ$, $U = 9883(8)$ Å³, $Z = 8$, $D_m = 1.47(1)$, $D_c = 1.516$ g cm⁻³, $\mu(Mo-K\alpha) = 20.0$ cm⁻¹, $F(000) = 4664$. Intensity data were measured at 290(1) K with Mo-K α radiation (graphite crystal monochromator) using an Enraf-Nonius CAD-4F diffractometer and employing the $\omega/2\theta$ scan method. The structure was solved from the Patterson function (SHELXS-86) and refined by means of blocked full-matrix least-squares procedure (SHELX-76), with anisotropic thermal parameters assigned to all non-hydrogen atoms except those of the methanol molecules of solvation; one of the methanols of crystallisation is disordered across a centre of symmetry. A difference map revealed almost all of the hydrogen atoms of the macrocycle. All the hydrogen atoms of the macrocycle as well as those of other coordinated species (excluding the OH) were included in the model at their calculated positions. At convergence $R = 0.046$ and $R_w = 0.044$ for the 1471 observed reflections [$I \geq 2.5\sigma(I)$]. 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.

resembles the above solid state arrangement. Two different types of acetate units in 1:2 proportions are indicated by the appearance in the ^1H spectrum of two separate singlets at δ 0.97 (3H of bridging acetate) and 2.07 (6H of two monodentate acetates). The ^{13}C spectrum also indicates two types of acetates [δ 22.66 and 23.04 (methyls) and 179.01 and 179.55 (carboxylates)]. All sixteen hydrogens of the methylene units are inequivalent in the solid state structure and the region of the ^1H NMR spectrum corresponding to these groups is complicated.

Preliminary studies indicate that L^{4-} readily binds a wide range of metal species other than Zn^{2+} to give not only tetranuclear complexes but also trinuclear and binuclear complexes, e.g. the binuclear LB_2O_8 is readily isolated in pure, crystalline form directly from the reaction mixture of **1** with excess NaBH_4 in methanolic solution. In conclusion this

new type of ligand appears to be both chemically robust and very versatile, giving a wide range of complexes which promise interesting new chemistry.

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§ Satisfactory analyses and mass spectra.