# Dinuclear Zinc(II) Complexes of a Robson Macrocycle†

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Dinuclear zinc(II) complexes of the Robson macrocycle $H_2L$, derived from the cyclocondensation of 2,6-diformyl-4-methylphenol and propane-1,3-diamine have been synthesised and their crystal structures determined. The compound $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$ crystallises in the monoclinic space group $P2_1/a$ ($C^5_{2h}$ no. 14) with $a$ = 14.755(15), $b$ = 12.348(12), $c$ = 16.825(17) Å, β = 105.80(3)° and $Z$ = 4. The crystal structure consists of two independent pairs of dinuclear zinc complexes (molecules 1 and 2). Molecule 1 contains two six-co-ordinate zinc(II) with an intermetallic distance of 3.166 Å, and molecule 2 has two five-co-ordinate zinc(II) with a Zn ··· Zn distance of 3.177 Å. The compound $[Zn_2(L)(N_3)_2]$ crystallises in the monoclinic space group $P2_1/c$ ($C^5_{2h}$, no 14) with $a$ = 7.733(5), $b$ = 11.865(6), $c$ = 14.466(4) Å, β = 90.86(4)° and $Z$ = 2. The two zinc atoms are five-co-ordinate and are separated by 3.333 Å.

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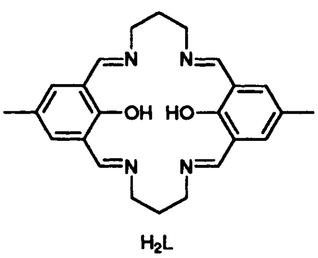
In 1970 Pilkington and Robson[1] synthesised a novel series of homodinuclear macrocyclic complexes of the type $[M_2(L)Cl_2]$ (M = $Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$ or $Zn^{II}$, L = the dianion of $H_2L$). The complexes were synthesised by cyclocondensation of 2,6-diformyl-4-methylphenol and propane-1,3-diamine in the presence of the requisite metal ion which functioned as a template.

On the basis of magnetic and spectroscopic evidence the complexes were assigned structures in which the cations were in approximately square-pyramidal geometries. This was confirmed by the crystal structure of $Cu_2(L)Cl_2 \cdot 6H_2O$ which also showed that the configuration of the macrocyclic ligand was approximately planar and that the anions were disposed on either side of the ring. These observations led to the proposal that L has the ability to impose a square-pyramidal geometry on metal ions which are unsuited to five-co-ordination.

As part of an inquiry into dinuclear zinc complexes we have prepared the complexes $Zn_2(L)X_2$ ($X = ClO_4^-, N_3^-$ or $NO_3^-$) by a modified synthetic pathway and determined the crystal structures of $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$ and $[Zn_2(L)(N_3)_2]$ in order to determine whether the above proposal concerning geometric imposition holds true for zinc.

## Results and Discussion

Traditionally dinuclear complexes of Robson macrocycles are prepared by a template procedure.[1,2] A convenient synthetic method, with high yields, is provided here for such complexes (Scheme 1). Sodium 2,6-diformyl-4-methylphenolate readily forms a [2 + 2] macrocyclic Schiff base with propane-1,3-diamine;[3] this disodium complex ($Na_2L$) of the Robson macrocycle ($H_2L$) then readily undergoes transmetallation by transition metals to form dinuclear macrocyclic complexes. The dinuclear zinc complex, $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$, was therefore prepared by refluxing a suspended ethanolic solution of $Na_2L$ with $Zn(ClO_4)_2 \cdot 6H_2O$ in ethanol for 1 h. On cooling the solution yellow crystals of the product were recovered. The nitrato complex was similarly prepared fron zinc nitrate and the azido complex was prepared by first forming the acetato complex and then reacting this complex with sodium azide.



$H_2L$

The crystal structure of $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$ consists of two independent pairs of dinuclear zinc complexes (molecules 1 and 2), each possessing a centre of symmetry between the metal ions. Two perchlorate counter ions and two water molecules are associated with each bimetallic macrocyclic dication. The molecular structures, each comprising a [2 + 2] Schiff-base macrocycle derived from O-deprotonated 2,6-diformyl-4-methylphenol and propane-1,3-diamine, are illustrated in Figs. 1 (molecule 1) and 2 (molecule 2), each with atom labelling. Bond lengths and angles with estimated standard deviations are listed in Table 1 and the atomic coordinates are given in Table 2.

Molecule 1 contains two six-co-ordinate zinc(II) with an intermetallic distance of 3.166 Å, and Zn–O–Zn angle of 101.7°. The co-ordination geometry of the zinc is derived from four macrocyclic ligand donors (the two symmetry related phenolic oxygens and the intervening pair of imine nitrogens), a water molecule and a more distant monodentate perchlorate anion, [Zn(1)–O(1) and Zn(1)–O(1A) 2.039, 2.043, Zn(1)–N(1) 2.029, Zn(1)–N(2) 2.035, Zn(1)–O(2) 2.103 and Zn(1)–O(3) 2.662 Å]. The co-ordination geometry at each metal may be regarded as distorted octahedral [O(1), O(1A), N(1), N(2) plane, root mean square (r.m.s.) deviation 0.000 with Zn(1) −0.222, O(2) −2.319 and O(3) 2.427 Å, out of plane].

The metal co-ordination geometry for molecule 2 is derived from four macrocyclic ligand donors and a water molecule only with the corresponding perchlorate anion in a more remote position than in molecule 1 [Zn(2)–O(7) and Zn(2)–O(7A) 2.050, 2.046, Zn(2)–N(3) 2.048, Zn(2)–N(4) 2.032, Zn(2)–O(8) 2.112 and Zn(2) ··· O(10) 3.042 Å], and with a Zn ··· Zn distance of 3.177 Å and Zn–O–Zn angle of 101.8°. For molecule 2 the co-ordination geometry at each metal may be considered as distorted square pyramidal [O(7), O(7A), N(3), N(4) plane, r.m.s. deviation 0.039 Å, with Zn(2) −0.287, O(8) −2.390 and a more distant O(10) at 2.741 Å out of plane].

The phenyl rings are each planar (r.m.s. deviations 0.001, 0.011 Å); in each case, the deviations of the oxygen and methyl

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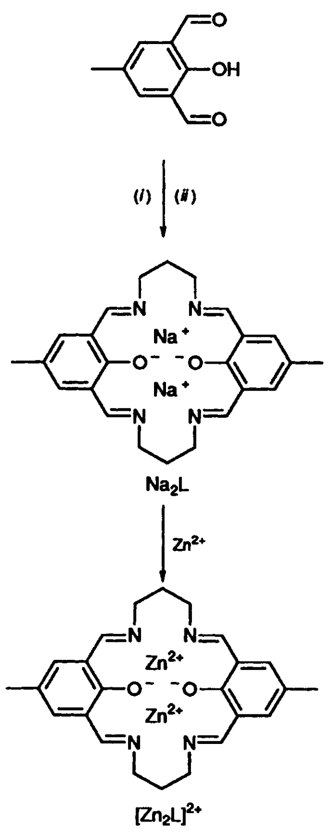
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 (*i*) NaOH; (*ii*) $H_2N(CH_2)_3NH_2$

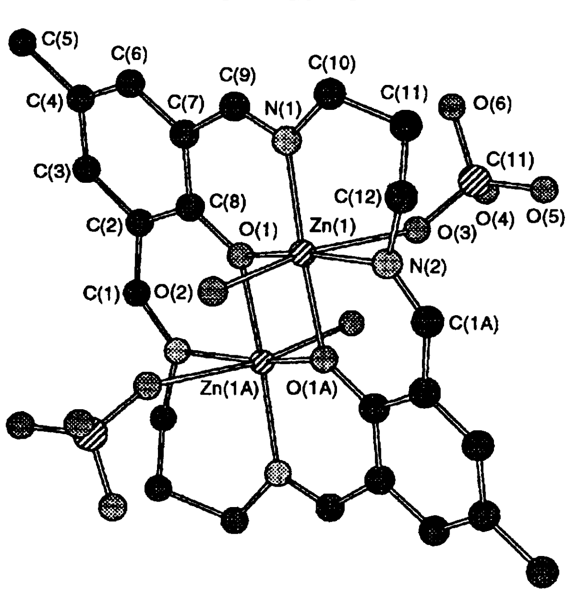


Fig. 1 Molecular structure of $Zn_2(L)(ClO_4)_2{\cdot}2H_2O$ (molecule 1)

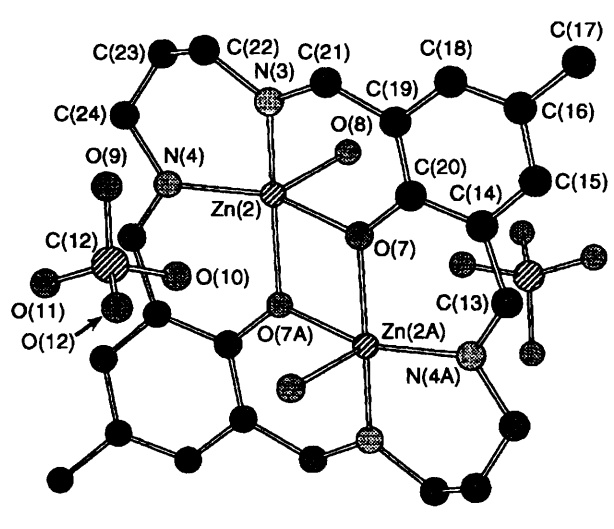


Fig. 2 Molecular structure of $Zn_2(L)(ClO_4)_2{\cdot}2H_2O$ (molecule 2)

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for $Zn_2(L)(ClO_4)_2{\cdot}2H_2O$

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 2.039(5) | Zn(1)–O(2) | 2.103(6) |
| Zn(1)–O(3) | 2.662(9) | Zn(1)–N(1) | 2.029(6) |
| Zn(1)–N(2) | 2.035(6) | Zn(1) ··· Zn(1A) | 3.166(4) |
| Zn(1)–O(1A) | 2.043(5) | Zn(2)–O(7) | 2.050(5) |
| Zn(2)–O(8) | 2.112(5) | Zn(2)–N(3) | 2.048(6) |
| Zn(2)–N(4) | 2.032(6) | Zn(2) ··· Zn(2A) | 3.177(4) |
| Zn(2) ··· O(10) | 3.042 | Zn(2)–O(7A) | 2.046(5) |
| O(1)–Zn(1)–O(2) | 94.5(2) | O(1)–Zn(1)–O(3) | 82.5(2) |
| O(2)–Zn(1)–O(3) | 170.1(2) | O(1)–Zn(1)–N(1) | 89.7(2) |
| O(2)–Zn(1)–N(1) | 100.1(2) | O(3)–Zn(1)–N(1) | 89.3(3) |
| O(1)–Zn(1)–N(2) | 164.1(2) | O(2)–Zn(1)–N(2) | 97.2(2) |
| O(3)–Zn(1)–N(2) | 84.1(3) | N(1)–Zn(1)–N(2) | 98.6(2) |
| O(3)–Zn(1)–Zn(1A) | 77.4(2) | O(2)–Zn(1)–Zn(1A) | 94.3(2) |
| N(2)–Zn(1)–Zn(1A) | 128.8(2) | N(1)–Zn(1)–Zn(1A) | 128.0(2) |
| O(2)–Zn(1)–O(1A) | 92.2(2) | O(1)–Zn(1)–O(1A) | 78.3(2) |
| N(1)–Zn(1)–O(1A) | 163.5(2) | O(3)–Zn(1)–O(1A) | 78.0(2) |
| O(7)–Zn(2)–N(3) | 89.4(2) | N(2)–Zn(1)–O(1A) | 90.6(2) |
| O(7)–Zn(2)–N(4) | 159.7(2) | O(7)–Zn(2)–O(8) | 94.2(2) |
| N(3)–Zn(2)–N(4) | 97.0(2) | O(8)–Zn(2)–N(3) | 97.7(2) |
| O(8)–Zn(2)–Zn(2A) | 96.1(2) | O(8)–Zn(2)–N(4) | 104.0(2) |
| N(4)–Zn(2)–Zn(2A) | 127.9(2) | N(3)–Zn(2)–Zn(2A) | 127.4(2) |
| O(8)–Zn(2)–O(7A) | 95.3(2) | O(7)–Zn(2)–O(7A) | 78.2(2) |
| N(4)–Zn(2)–O(7A) | 90.9(2) | N(3)–Zn(2)–O(7A) | 162.7(3) |
| Zn(1)–O(1)–C(8) | 129.3(4) | Zn(1)–O(1)–Zn(1A) | 101.7(2) |
| C(8)–O(1)–Zn(1A) | 128.2(4) | Zn(1)–O(3)–Cl(1) | 148.0(5) |
| Zn(2)–O(7)–C(20) | 127.0(4) | Zn(2)–O(7)–Zn(2A) | 101.8(2) |
| C(20)–O(7)–Zn(2A) | 128.8(4) | Zn(1)–N(1)–C(9) | 123.0(4) |
| Zn(1)–N(1)–C(10) | 121.0(5) | Zn(1)–N(2)–C(1A) | 124.2(5) |
| Zn(1)–N(2)–C(12) | 117.7(5) | Zn(2)–N(3)–C(21) | 121.5(5) |
| Zn(2)–N(3)–C(22) | 120.8(5) | Zn(2)–N(4)–C(13A) | 124.1(5) |
| Zn(2)–N(4)–C(24) | 120.2(5) | | |

carbons are small (less than 0.023 Å). However, the imines 'twist' out of the planes in opposite directions [deviations of nitrogens −0.014, 0.048 Å for molecule 1 and −0.062, 0.159 Å for molecule 2; corresponding to a set of (O)CCC=N torsion angles of −1.4, −7.1°; −3.0, −7.6°].

The central carbon, C(11), of the diiminopropane fragment of the macrocycle in molecule 1, is disordered between two positions with unequal site occupancy factors (0.8285 and 0.1715). The equivalent atom for molecule 2, C(23), shows only high thermal vibration approximately parallel to the crystallographic *a* axis. The zinc–diiminopropane six-membered chelate rings each have an approximately planar 'central' group of four atoms (N–C ··· C–N) with both boat and chair conformations evident [r.m.s. deviations of four-atom fragments 0.065 and 0.037 Å, with Zn(1) −0.177, C(11) 0.629, C(11A) −0.556 Å and Zn(2) 0.178, C(23) 0.408 Å out of the planes for molecules 1 and 2 respectively].

The mean plane of the two independent macrocycles lies approximately parallel (10.0°), mutually rotated (angle between Zn ··· Zn intramolecular vectors 67°) and separated along the crystallographic *c* axis by approximately 4 Å (Fig. 3), but laterally 'sheared' by approximately the breadth of a macrocycle, such that in projection perpendicular to the $Zn_2O_2$ plane there is very little overlay of macrocycles. Water molecules are involved in intra- and inter-molecular hydrogen

**Table 2** Atom coordinates ( × $10^4$) for $Zn_2(L)(ClO_4)_2\cdot 2H_2O$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Zn(1) | 108(1) | 1162(1) | 413(1) |
| Zn(2) | −181(1) | 950(1) | 4339(1) |
| Cl(1) | 2655(1) | 1231(2) | 137(1) |
| Cl(2) | −3103(1) | 662(2) | 4079(1) |
| O(1) | −308(3) | 439(3) | −718(3) |
| O(2) | −1246(3) | 1157(4) | 596(3) |
| O(3) | 1816(5) | 802(6) | 225(6) |
| O(4) | 3005(6) | 558(8) | −356(7) |
| O(5) | 3314(6) | 1397(7) | 891(5) |
| O(6) | 2466(5) | 2263(6) | −231(5) |
| O(7) | 88(3) | 702(3) | 5586(3) |
| O(8) | 1248(3) | 1197(4) | 4382(3) |
| O(9) | −3121(5) | 1815(4) | 4004(4) |
| O(10) | −2154(5) | 318(6) | 4397(5) |
| O(11) | −3457(7) | 211(6) | 3297(5) |
| O(12) | −3601(6) | 363(7) | 4636(7) |
| N(1) | 88(4) | 2623(4) | −144(4) |
| N(2) | 828(4) | 1597(4) | 1581(4) |
| N(3) | −515(4) | 2528(4) | 4505(4) |
| N(4) | −842(4) | 863(5) | 3112(4) |
| C(1) | −1175(4) | −932(6) | −2155(4) |
| C(2) | −1155(4) | 243(5) | −2147(4) |
| C(3) | −1606(5) | 740(6) | −2901(5) |
| C(4) | −1666(5) | 1862(6) | −3001(5) |
| C(5) | −2154(5) | 2376(7) | −3818(5) |
| C(6) | −1248(5) | 2466(6) | −2311(5) |
| C(7) | −786(4) | 2025(5) | −1539(4) |
| C(8) | −731(4) | 867(5) | −1444(4) |
| C(9) | −344(4) | 2790(5) | −905(5) |
| C(10) | 486(5) | 3601(5) | 341(5) |
| C(11) | 1201(7) | 3397(7) | 1139(5) |
| C(11A) | 431(28) | 3585(26) | 1198(11) |
| C(12) | 937(7) | 2763(6) | 1771(5) |
| C(13) | 1055(5) | 26(6) | 7289(4) |
| C(14) | 848(4) | 1132(6) | 7003(4) |
| C(15) | 1172(5) | 1933(6) | 7602(5) |
| C(16) | 1028(5) | 3032(6) | 7440(5) |
| C(17) | 1379(6) | 3868(7) | 8104(6) |
| C(18) | 557(5) | 3288(6) | 6657(5) |
| C(19) | 234(4) | 2537(5) | 6012(5) |
| C(20) | 385(4) | 1429(5) | 6179(4) |
| C(21) | −234(5) | 2993(5) | 5215(5) |
| C(22) | −999(7) | 3197(7) | 3804(5) |
| C(23) | −947(12) | 2849(8) | 3043(7) |
| C(24) | −1185(7) | 1850(7) | 2643(5) |

**Table 3** Selected bond lengths (Å) and angles (°) with e.s.d.s for $[Zn_2(L)(N_3)_2]$

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 2.076(6) | Zn(1)–N(1) | 2.047(8) |
| Zn(1)–N(2) | 2.109(8) | Zn(1)–N(3) | 2.095(8) |
| Zn(1)–O(1A) | 2.126(6) | Zn(1) ··· Zn(1A) | 3.333(3) |
| O(1)–Zn(1)–N(1) | 107.4(3) | O(1)–Zn(1)–N(2) | 88.4(3) |
| N(1)–Zn(1)–N(2) | 104.7(3) | O(1)–Zn(1)–N(3) | 148.5(3) |
| N(1)–Zn(1)–N(3) | 102.2(3) | N(2)–Zn(1)–N(3) | 94.5(3) |
| O(1)–Zn(1)–O(1A) | 75.0(3) | N(1)–Zn(1)–O(1A) | 104.8(3) |
| N(2)–Zn(1)–O(1A) | 149.3(3) | N(3)–Zn(1)–O(1A) | 87.3(3) |
| Zn(1)–O(1)–Zn(1A) | 105.0(3) | Zn(1)–O(1)–C(1) | 128.0(5) |
| Zn(1)–N(1)–N(4) | 120.2(7) | C(1)–O(1)–Zn(1A) | 127.0(5) |
| Zn(1)–N(2)–C(8) | 119.0(6) | Zn(1)–N(2)–C(7) | 125.1(6) |
| Zn(1)–N(3)–C(10) | 119.4(6) | Zn(1)–N(3)–C(12) | 125.5(6) |

bonding with symmetry related perchlorate anions [O(2) ··· O($3^{I}$) 2.799, H(O2B) ··· O($3^{I}$) 2.027, O(2) ··· O($6^{II}$) 2.813, H(O2A) ··· O($6^{II}$) 1.825, O(8) ··· O($9^{III}$) 2.760, H(O8A) ··· O($9^{III}$) 1.760, O(8) ··· O($10^{IV}$) 2.829, H(O8B) ··· O($10^{IV}$) 2.245 Å, with corresponding symmetry operations: I $-x,-y,-z$; II $x-0.5, 0.5-y, z$; III $x+0.5, -y, z$ and IV $-x, -y, 1-z$].

The molecular structure of $[Zn_2(L)(N_3)_2]$ is illustrated in Fig. 4; bond lengths and angles with estimated standard deviations are given in Table 3 and atomic coordinates are listed in Table 4. The bimetallic macrocycle is centrosymmetric and comprises two related zinc(II) ions which are asymmetrically bridged by a symmetry related pair of phenolate oxygen atoms (Zn–O 2.076 and 2.126 Å): each zinc is also co-ordinated by two imino-nitrogen atoms, and carries a terminal azide ligand (Zn–N–N 120, N–N–N 175°). The zinc–zinc separation is 3.333 Å and each zinc has a square-based pyramidal co-ordination geometry, with mutually *cis*-basal bridging oxygens [r.m.s. deviation through O(1),O(1A),N(2),N(3) 0.000 Å, displacement of zinc 0.532 Å], and the azido nitrogen N(1) in the axial site at a greater displacement (2.577 Å), the Zn–N bond length being 2.047 Å. The phenolic ring is planar (r.m.s. deviation 0.013 Å), with a deviation of the methyl carbon by only 0.062 Å, and of O(1), C(7) and C(12A) by 0.019, 0.017 and −0.096 Å respectively. There are no significant intermolecular contacts, and no opportunities for hydrogen bonding.

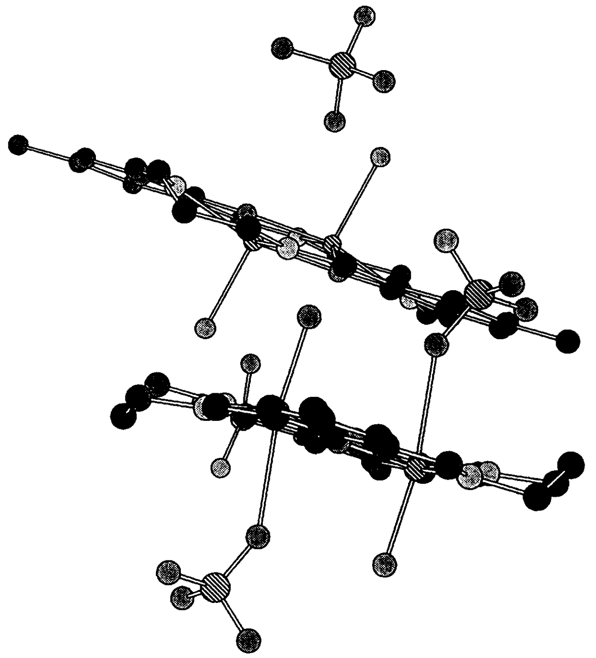


**Fig. 3** View, perpendicular to the *c* axis, of molecules 1 (lower) and 2 (upper) of $Zn_2(L)(ClO_4)_2\cdot 2H_2O$

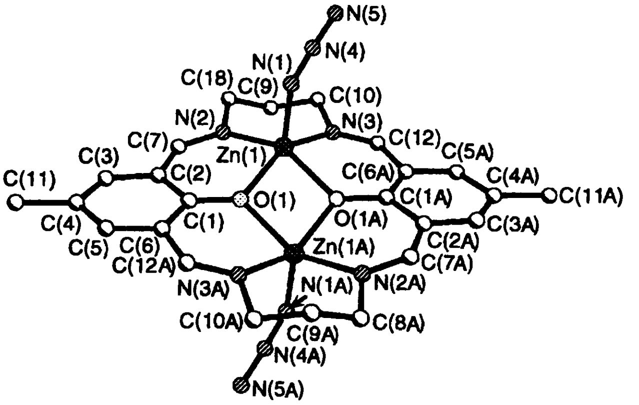


**Fig. 4** Molecular structure of $[Zn_2(L)(N_3)_2]$

The $^1H$ NMR spectra of the nitrato- and perchlorato-complexes show that the integrity of the ligand is maintained in methanolic solution.

Di- and tri-nuclear zinc species exist in a variety of enzymes containing zinc-active sites. For instance alkaline phosphatase, which catalyses non-specific hydrolysis of phosphate monoesters,[4] P1 nuclease,[5] leucine aminopeptidase[6] and phospholipase C, which cleave phospholipids by

**Table 4** Atom coordinates ( × $10^4$) for $[Zn_2(L)(N_3)_2]$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Zn(1) | 420(1) | 1369(1) | 128(1) |
| O(1) | 1296(7) | −68(5) | −536(4) |
| N(1) | −956(11) | 2293(7) | −825(6) |
| N(2) | 2955(10) | 2018(6) | 73(5) |
| N(3) | −170(10) | 2185(6) | 1368(5) |
| N(4) | −1543(11) | 3170(8) | −620(7) |
| N(5) | −2226(17) | 4014(10) | −449(9) |
| C(1) | 2662(11) | −170(7) | −1089(6) |
| C(2) | 4100(11) | 624(7) | −1042(6) |
| C(3) | 5522(11) | 471(8) | −1632(6) |
| C(4) | 5619(12) | −359(8) | −2312(7) |
| C(5) | 4199(12) | −1109(7) | −2353(6) |
| C(6) | 2763(11) | −1050(7) | −1762(6) |
| C(7) | 4193(12) | 1599(7) | −414(6) |
| C(8) | 3348(14) | 3138(9) | 532(8) |
| C(9) | 2652(15) | 3229(10) | 1473(8) |
| C(10) | 769(14) | 3265(9) | 1625(8) |
| C(11) | 7150(14) | −438(10) | −2984(8) |
| C(12) | −1485(12) | 1960(8) | 1885(7) |

hydrolysis,[7] all contain trinuclear constellations in which a pair of zinc atoms have been found to be bridged by oxygen with separations in the range 2.88–3.94 Å. Although the co-ordination number of zinc ranged from 4 to 6, ligand atoms are both nitrogen and oxygen in these enzymes. Molecule 2 of $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$ studied here may therefore serve as a simple structural model for dinuclear portions of the trinuclear constellations found in phospholipase C and P1 nuclease (Fig. 5) both of which contain a pair of five-co-ordinated zinc atoms separated by *ca.* 3.2 Å together with a third five-co-ordinated zinc atom some 5 Å from the pair. Furthermore both zinc atoms have co-ordinated water molecules which are likely to be polarised and therefore capable of initiating nucleophilic attack on a substrate molecule as has been proposed in the mode of action for several hydrolytic zinc enzymes.

Molecule 2 may also be compared with the dizinc cation in the dizinc complex of the acyclic ligand 2,6-bis[bis(benzimidazol-2-ylmethyl)aminomethyl]-4-methylphenol (Hbbap), $[Zn_2(bbap)(H_2O)_2(\mu\text{-}OCH_2Ph)][ClO_4]_2 \cdot 4MeOH$.[8] In this complex one zinc is in an octahedral environment and the second is five-co-ordinated and the observation of this unusual co-ordination geometry led to the suggestion that the complex can act as a model for the transition state of the catalytic process of phospholipase C.[8] In a preliminary study, albeit hampered by poor solubility, we were unable to detect any promotion of the hydrolysis of either tris(4-nitrophenyl) phosphate or bis(4-nitrophenyl) phosphate by either of the dinuclear zinc complexes derived from the Robson macrocycle.

## Experimental

Elemental analyses were carried out by the University of Sheffield microanalytical service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1710 Fourier-transform infrared spectrophotometer. Proton NMR spectra were recorded using a Bruker AM-250 spectrometer. Positive-ion FAB mass spectra were recorded on a Kratos MS25 spectrometer with 3-nitrobenzyl alcohol as the matrix solvent.

*Preparation of* $Na_2L$.—Propane-1,3-diamine [1 mmol in ethanol (10 $cm^3$)] was added slowly to a suspension of sodium 2,6-diformyl-4-methylphenolate (1 mmol) in ethanol (20 $cm^3$). The mixture was stirred under reflux for 1 h and the resulting yellow product was filtered off and dried under vacuum. The yield of the disodium complex was 90% (Found: C, 64.05; H, 5.95; N, 12.15. $C_{24}H_{26}N_4Na_2O_2$ requires C, 64.30; H, 5.85; N, 12.50%); IR (KBr disc): $\nu_{C=N}$ 1632 $cm^{-1}$. Mass spectrum (positive-ion FAB), *m/z* 427 $[NaL]^+$.

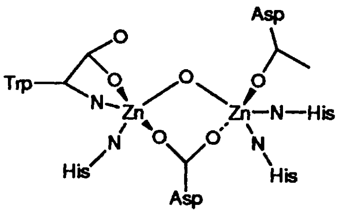


**Fig. 5** Schematic representation of the dinuclear portion of the binding site in phospholipase C and P1 nuclease; His, Asp and Trp are histidine, aspartic acid and tryptophan residues

*Transmetallation of* $Na_2L$ *with Zinc Perchlorate or Nitrate*.—The compound $Na_2L$ (1 mmol) was suspended in ethanol (30 $cm^3$) and the appropriate zinc salt (2 mmol) added. The mixture was refluxed for 1 h, filtered hot and left to cool. The dizinc complexes crystallised out in 80–90% yield and were dried under vacuum. The crystallographic sample of $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$ was obtained by recrystallisation from ethanol–methanol (1 : 1).

$Zn_2(L)(ClO_4)_2 \cdot 2H_2O$ (Found: C, 37.80; H, 4.25; N, 7.30. $C_{24}H_{26}Cl_2N_4O_{10}Zn_2 \cdot 2H_2O$ requires C, 37.55; H, 3.95; N, 7.30%); IR(KBr disc) $\nu_{C=N}$ 1641 $cm^{-1}$. Mass spectrum (positive-ion FAB), *m/z* 631 $[Zn_2L(ClO_4)]^+$; $^1H$ NMR($CD_3OD$) δ 8.45 (s, 4 H, HC=N), 7.48 (s, 4 H, aromatic H), 4.05 (t, 8 H, $CH_2$), 2.31 (s, 6 H, $CH_3$), 2.18 (m, 4 H, $CH_2$).

$Zn_2(L)(NO_3)_2 \cdot H_2O$ (Found: C, 43.20; H, 4.35; N, 12.05. $C_{24}H_{26}N_6O_8Zn_2 \cdot H_2O$ requires C, 42.70; H, 4.20; N, 12.45%); IR(KBr disc) $\nu_{C=N}$ 1637 $cm^{-1}$. Mass spectrum (positive-ion FAB), *m/z* 592 $[Zn_2L(NO_3)]^+$; $^1H$ NMR($CD_3OD$) δ 8.35 (s, 4 H, HC=N), 7.40 (s, 4 H, aromatic H), 3.95 (t, 8 H, $CH_2$), 2.25 (s, 6 H, $CH_3$), 2.10 (m, 4 H, $CH_2$).

The azide complex was prepared by first using zinc acetate in the above procedure and then adding excess of sodium azide to effect anion metathesis. The bulk sample was recovered in 64% yield. The crystallographic sample was obtained by recrystallisation from dimethylformamide.

$Zn_2(L)(N_3)_2 \cdot H_2O$ (Found: C, 45.45; H, 4.35; N, 22.35. $C_{24}H_{26}N_{10}O_2Zn_2 \cdot H_2O$ requires C, 45.35; H, 4.45; N, 22.05%); IR (KBr disc) $\nu_{N=N}$ 2091, $\nu_{C=N}$ 1636 $cm^{-1}$. Mass spectrum (positive-ion FAB), *m/z* 575 $[Zn_2L(N_3)]^+$.

*Crystal Structure Determinations*.—*Crystal data for* $[Zn_2(L)(N_3)_2]$. $C_{24}H_{26}N_{10}O_2Zn_2$, $M = 617.29$. Crystallises from dimethylformamide as pale yellow blocks; crystal dimensions 0.70 × 0.25 × 0.25 mm. Monoclinic, $a = 7.733(5)$, $b = 11.865(6)$, $c = 14.466(4)$ Å, $\beta = 90.86(4)°$, $U = 1327.1(11)$ Å$^3$, $Z = 2$, $D_c = 1.545$ g $cm^{-3}$, space group $P2_1/c$ ($C^5_{2h}$, no 14), Mo-Kα radiation ($\bar{\lambda} = 0.710\,69$ Å), $\mu$(Mo-Kα) = 18.93 $cm^{-1}$, $F(000) = 631.79$.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the omega scan method. The 1467 independent reflections (of 2759 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 6 azimuthal scans (minimum and maximum transmission coefficients 0.118 and 0.166). The structure was solved by direct methods and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0795$ ($R' = 0.0747$, 172 parameters, mean and maximum $\delta/\sigma$ 0.015 and 0.069), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.73 and 0.89 e Å$^{-3}$. A weighting scheme $w^{-1} = \sigma^2(F) + 0.001\,04\,(F)^2$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[9] as implemented on a Data General DG30 computer.

*Crystal data for* $Zn_2(L)(ClO_4)_2 \cdot 2H_2O$. $C_{24}H_{30}Cl_2N_4O_{12}Zn_2$, $M = 768.20$. Crystallises from ethanol–methanol

(1:1) as yellow prismatic crystals; crystal dimensions 0.74 × 0.35 × 0.21 mm. Monoclinic, $a = 14.755(15)$, $b = 12.348(12)$, $c = 16.825(17)$ Å, $\beta = 105.80(3)°$, $U = 2950(5)$ Å$^3$, $Z = 4$, $D_c = 1.74$ g cm$^{-3}$, space group $P2_1/a$ ($C^5_{2h}$, no. 14), Mo-K$\alpha$ radiation ($\bar{\lambda} = 0.710\,69$ Å), $\mu$(Mo-K$\alpha$) = 19.16 cm$^{-1}$, $F(000) = 1567.69$.

Three-dimensional, room-temperature X-ray data were collected in the range $6.5 < 2\theta < 50.0°$ on a Stoe Stadi 2 diffractometer by the omega scan method. The 3419 independent reflections (of 5645 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption (minimum and maximum transmission coefficients 0.5080 and 0.6999). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Anisotropic refinement was allowed for all non-hydrogen atoms with the exception of a minor fractional occupancy carbon atom [C(11A), occupancy factor 0.1715] of a diamine molecule fraction. Refinement converged at a final $R = 0.0576$ (403 parameters, mean and maximum $\delta/\sigma$ 0.006 and 0.020), minimum and maximum final electron density $-0.736$ and 0.807 e Å$^{-3}$ close to the metal atoms. Complex scattering factors were taken from the program package SHELXTL[9] as implemented on a Data General DG30 computer. Unit weights were employed.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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