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Zinc(II) complexes of tetrapodal ligands derived from tetra-substituted 1,*n*-diaminoalcohols

Harry Adams, Darren Bradshaw and David E. Fenton*

Department of Chemistry, Dainton Building, The University of Sheffield, Sheffield, UK S3 7HF. E-mail: d.fenton@sheffield.ac.uk

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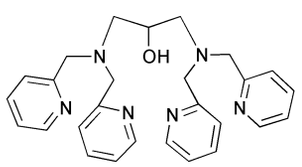
Dinuclear zinc(II) complexes have been prepared from one non-symmetric and two symmetric compartmental ligands in which the pendant arms, bearing pyridyl and phenolic functions, are bridged by spacers derived from 1,*n*-diaminoalcohols. The X-ray crystal structures of four complexes $[Zn_2L^1(OAc)](ClO_4)_2\cdot CH_3OH$ (**1a**), $[Zn_2L^1(OAc)](BPh_4)_2\cdot 6H_2O$ (**2a**), $[Zn_2L^2(OAc)](PF_6)_2$ (**4a**) and $[Zn_2L^3(OAc)]\cdot 2.5H_2O\cdot 1.5CH_3OH$ (**8a**) are reported.

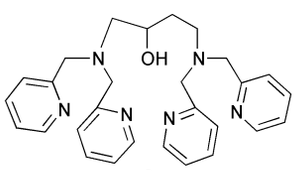
Introduction

A number of polypodal pro-ligands derived from 1,*n*-diaminoalcohols and bearing pyridyl,[1–9] phenolic,[10–12] 6-methylpyridyl[13,14] and 1-ethylbenzimidazolyl[15,16] groups have been synthesised and used to prepare a range of dinuclear transition metal complexes. The most widely studied of the pro-ligands is HL^1 which has been used in modelling studies related to the metallobiosites involved in PSII[1–4] and hydrolases,[7,8] and for dioxygen binding studies.[5,6]

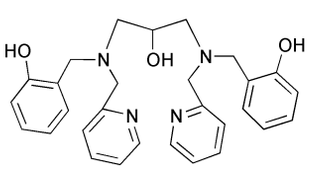
A dinuclear Zn(II) complex of HL^1 has been shown to hydrolyse a phosphodiester linkage in a diribonucleotide under mild conditions.[8] The rate of hydrolysis of the substrate, adenylyl-(3′-5′)adenosine (ApA) is largely dependent on the $[ZnCl_2]$: $[HL^1]$ ratio and is at a maximum when equal to two. This suggests that a dinuclear complex is the active species. Although the formation of a stable complex between $ZnCl_2$ and HL^1 was evidenced by ^1H NMR the complex was not isolated and so the exact nature of the species was not established.



HL^1



HL^2



H_3L^3

In the present work the symmetrical compartmental pro-ligands HL^1, bearing two N_3O donor sets, and HL^3 with two N_2O_2 donor sets, and the non-symmetrical pro-ligand HL^2, with two N_3O donor sets, have been reacted with zinc(II) acetate in the presence of counter-anions to facilitate crystallisation in order to investigate the effect of changes in the ligand framework and donor provision on the structure of the product. The X-ray crystal structures of four complexes $[Zn_2L^1(OAc)](ClO_4)_2\cdot CH_3OH$ (**1a**), $[Zn_2L^1(OAc)](BPh_4)_2\cdot 6H_2O$ (**2a**), $[Zn_2L^2(OAc)](PF_6)_2$ (**4a**) and $[Zn_2L^3(OAc)]\cdot 2.5H_2O\cdot 1.5CH_3OH$ (**8a**) are reported.

Experimental

Elemental analyses were carried out by the University of Sheffield microanalytical service. Positive ion fast atom bombardment (FAB) mass spectra were recorded using a VG ProSpec spectrometer (the matrix used was 4-nitrobenzyl alcohol). IR spectra were recorded as KBr discs using a Perkin Elmer 1600 IR spectrophotometer.

Ligand synthesis

The pro-ligands were prepared by literature methods: 1,3-bis(bis-pyridin-2-ylmethylamino)propan-2-ol (HL^1),[17] 1,4-bis-(bis-pyridin-2-ylmethylamino)butan-2-ol (HL^2),[6] and 1,3-bis(2-hydroxybenzylpyridin-2-ylmethylamino)propan-2-ol (H_3L^3).[11]

Metal complexes of HL^1 and HL^2

The complexes were prepared by adding two equivalents of $Zn(OAc)_2\cdot 2H_2O$ to a warm methanolic solution of the pro-ligand (one equivalent) and NEt_3 (one equivalent). When dissolution was complete two equivalents of the alkali metal salt of the requisite counter-anion were added and the solution heated at reflux for 30 minutes. If no solid precipitated during the reaction then the solution was cooled to room temperature and left to crystallize. If a white solid precipitated upon addition of the anion this was removed by filtration, washed with cold MeOH and dried *in vacuo* prior to analysis. One problem encountered was that for the crystalline complexes the bulk analysis gave a different solvation number than the structural analysis of crystals. This occurred because the crystals were taken directly from the mother liquor for immediate mounting whereas the bulk samples were dried prior to analysis and so any volatile solvent was lost. *Caution!* Although we have experienced no difficulties with the perchlorate salts they should nevertheless be regarded as hazardous and treated with care.

$[Zn_2L^1(OAc)](ClO_4)_2\cdot 0.5CH_3OH$ (1). HL^1 (0.5 g. 1.1 mmol), $Zn(OAc)_2\cdot 2H_2O$ (0.48 g, 2.2 mmol), $NaClO_4\cdot H_2O$ (0.31 g, 2.2 mmol) and methanol (35 ml) were used. Yield, 0.45g (47%). Anal.(bulk sample) Calc. for $C_{29.5}H_{34}Cl_2N_6O_{11.5}Zn_2$: C, 41.3;

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H, 4.0; N, 9.8; Cl, 8.3. Found: C, 40.6; H, 3.9; N, 9.7; Cl, 8.9%. MS(FAB): *m*/*z*: 743 (100%) $[Zn_2L^1(OAc)(ClO_4)]^+$. IR (KBr disc, ν/cm^{-1}): 1610 (C=N-pyr), 1577 (C=C-Ar), 1555 (ν_{as}OAc), 1440 (ν_sOAc), 1087 (ClO_4). Crystals suitable for X-ray analysis (**1a**) were obtained from methanol.

$[Zn_2L^1(OAc)](BPh_4)_2$ (2). HL^1 (56 mg. 0.12 mmol), $Zn(OAc)_2\cdot 2H_2O$ (52 mg, 0.24 mmol), $NaBPh_4$ (82 mg, 0.24 mmol) and methanol (10 ml) were used. Yield, 64 mg (42%). Anal.(bulk sample) Calc. for $C_{77}H_{72}B_2N_6O_3Zn_2$: C, 72.1; H, 5.7; N, 7.8. Found: C, 71.0; H, 5.5; N, 6.6% IR (KBr disc, ν/cm^{-1}): 1609 (C=N-pyr), 1579 (C=C-Ar), 1561 (ν_{as}OAc), 1438 (ν_sOAc). Crystals suitable for X-ray analysis (**2a**) were obtained from methanol.

$[Zn_2L^1(OAc)](PF_6)_2$ (3). HL^1 (56 mg. 0.12 mmol), $Zn(OAc)_2\cdot 2H_2O$ (52 mg, 0.24 mmol), $KPF_6\cdot 6H_2O$ (44 mg, 0.24 mmol) and methanol (10 ml) were used. Yield, 67 mg (60%). Anal.(bulk sample) Calc. for $C_{29}H_{32}N_6O_3F_{12}P_2Zn_2$: C, 37.3; H, 3.5; N, 9.0. Found: C, 37.2; H, 3.3; N, 8.8%. MS(FAB): *m*/*z*: 789 (69%) $[Zn_2L^1(OAc)(PF_6)]^+$. IR (KBr disc, ν/cm^{-1}): 1614 (C=N-pyr), 1555 (ν_{as}OAc), 1449 (ν_sOAc), 832(PF_6).

$[Zn_2L^2(OAc)](PF_6)_2\cdot 4H_2O$ (4). HL^2 (172 mg. 0.37 mmol), $Zn(OAc)_2\cdot 2H_2O$ (161 mg, 0.24 mmol), $KPF_6\cdot 6H_2O$ (135 mg, 0.74 mmol) and methanol (10 ml) were used. Yield, 100 mg (30%). Anal.(bulk sample) Calc. for $C_{30}H_{42}N_6O_7F_{12}P_2Zn_2$: C, 35.3; H, 4.2; N, 8.2. Found: C, 35.4; H, 3.6; N, 7.7%. MS(FAB): *m*/*z*: 803 (37%) $[Zn_2L^2(OAc)(PF_6)]^+$. IR (KBr disc, ν/cm^{-1}): 1614 (C=N-pyr), 1584(C=C-Ar), 1567 (ν_{as}OAc), 1444 (ν_sOAc), 832(PF_6). Crystals suitable for X-ray analysis (**4a**) were obtained from methanol.

$[Zn_2L^2(OAc)](ClO_4)_2\cdot 2CH_3OH\cdot 2H_2O$ (5). HL^1 (0.51 g. 1.1 mmol), $Zn(OAc)_2\cdot 2H_2O$ (0.48 g, 2.2 mmol), $NaClO_4\cdot H_2O$ (0.31 g, 2.2 mmol) and methanol (10 ml) were used. Yield, 0.98g (12%). Anal.(bulk sample) Calc. for $C_{32}H_{46}Cl_2N_6O_{15}Zn_2$: C, 40.2; H, 4.8; N, 8.8; Cl, 7.4. Found: C, 40.1; H, 4.4; N, 8.6; Cl, 7.6%. MS(FAB): *m*/*z*: 757 (35%) $[Zn_2L^2(OAc)(ClO_4)]^+$. IR (KBr disc, ν/cm^{-1}): 1609 (C=N-pyr), 1579 (C=C-Ar), 1560 (ν_{as}OAc), 1442 (ν_sOAc), 1090 (ClO_4).

$[Zn_2L^2(OAc)](BPh_4)_2\cdot 0.5H_2O$ (6). HL^2 (101 mg. 0.22 mmol), $Zn(OAc)_2\cdot 2H_2O$ (97 mg, 0.44 mmol), $NaBPh_4$ (140 mg, 0.44 mmol) and methanol (10 ml) were used. Yield, 187 mg (65%). Anal.(bulk sample) Calc. for $C_{78}H_{75}B_2N_6O_{3.5}Zn_2$: C, 71.8; H, 5.8; N, 6.4. Found: C, 71.6; H, 5.4; N, 6.8%. MS(FAB): *m*/*z*: 978 (52%) $[Zn_2L^2(OAc)(BPh_4)]^+$. IR (KBr disc, ν/cm^{-1}): 1608 (C=N-pyr), 1582 (C=C-Ar), 1564 (ν_{as}OAc), 1437 (ν_sOAc).

Metal complexes of HL^3

The complexes were prepared in an analogous manner to those from HL^1 and HL^2 but without addition of an alkali metal salt.

$[Zn_2L^3(OAc)]\cdot 2H_2O$ (7). H_3L^3 (204 mg. 0.42 mmol), $Zn(OAc)_2\cdot 2H_2O$ (185 mg, 0.84 mmol) and methanol (10 ml) were used. Yield, 111 mg (38%). Anal.(bulk sample) Calc. for $C_{31}H_{36}N_4O_7Zn_2$: C, 52.6; H, 5.1; N, 7.9. Found: C, 52.7; H, 4.8; N, 7.7%. MS(FAB): *m*/*z*: 613 (43%) $[Zn_2L^3]^+$. IR (KBr disc, ν/cm^{-1}): 1604 (C=N-pyr), 1589 (C=C-Ar), 1568 (ν_{as}OAc), 1454 (ν_sOAc).

$[Zn_2L^3(OAc)]\cdot 5H_2O$ (8). H_3L^3 (204 mg. 0.42 mmol), $Zn(acac)_2\cdot xH_2O$ (221 mg, 0.84 mmol) and methanol (10 ml) were used. Yield, 71 mg (22%). Anal.(bulk sample) Calc. for $C_{31}H_{42}N_4O_{10}Zn_2$: C, 48.8; H, 5.6; N, 7.4. Found: C, 48.8; H, 5.4; N, 7.5%. MS(FAB): *m*/*z*: 613 (43%) $[Zn_2L^3]^+$. IR (KBr disc, ν/cm^{-1}): 1604 (C=N-pyr), 1587 (C=C-Ar), 1565 (ν_{as}OAc), 1451 (ν_sOAc). Crystals suitable for X-ray analysis (**8a**) were obtained from methanol.

X-Ray crystallography

Crystals of **1a**, **2a**, **4a**, and **8a** were obtained from methanol as colourless blocks, mounted on glass fibres and used for data collection. Single crystal X-ray diffraction data were collected using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) on a Siemens SMART CCD area detector with an Oxford Cryosystems low temperature system. Details of crystal data are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2; hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. In complex **1a** the perchlorate anion centred at Cl(3) and the methanol molecule were disordered and refined to occupancies of 54.1 : 45.9 and 60.8 : 39.2% respectively. In complex **2a** all six water molecules were disordered and refined to occupancies of 72.1 : 27.9 (O1W), 72.6 : 27.4 (O2W), 52.5 : 47.5 (O3W), 62.1 : 37.9 (O4W), 39.1 : 60.9 (O5W) and 60.3 : 39.7 % (O6W). In complex **4a** the two hexafluorophosphate anions centred on P(1) and P(2) were disordered and refined to occupancies of 40.1 : 59.9 and 9.8 : 90.2% respectively. In complex **8a** four of the attending water molecules were disordered and refined to occupancies of 44.5 : 55.5%. Weighting schemes (w) were used in the latter stages of refinement: complex **1a**, $w = 1/[\sigma^2(Fo^2) + (0.0712P)^2 + 0.00P]$; complex **2a**, $w = 1/[\sigma^2(Fo^2) + (0.1206P)^2 + 0.00P]$; complex **4a**, $w = 1/[\sigma^2(Fo^2) + (0.0897P)^2 + 0.00P]$; complex **8a**, $w = 1/[\sigma^2(Fo^2) + (0.1457P)^2 + 0.00P]$; $P = (Fo^2 + 2Fc^2)/3$ throughout. The crystal systems for **2a** and **8a** emulate an orthorhombic crystal setting. A hemisphere of data was collected for each system and equivalent reflections were analysed. This showed an unequivalent set of data points about the *b* axis indicating that the crystal sytem was monoclinic. Furthermore unsuccessful attempts were made to solve the structures in orthorhombic settings whereas solutions in the monoclinic crystal system converged successfully. Complex scattering factors were taken from the program package SHELXTL [18] as implemented on the Viglen Pentium computer.

CCDC reference numbers 173903–173906.

See http://www.rsc.org/suppdata/dt/b1/b110264h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Complexes derived from pro-ligand HL^1

Pro-ligand HL^1 forms complexes with $Zn(OAc)_2$ in the presence of weakly or non-coordinating counter-anions. The complexes are prepared in methanolic solution in the presence of triethylamine and have the general formula $[Zn_2L^1(OAc)](X)_2\cdot n$(solvent) where X = ClO_4^- (**1**), BPh_4^- (**2**) or PF_6^- (**3**). Complexes **1a** and **2a** crystallised as colourless blocks suitable for X-ray structural analysis from the methanolic solution after approximately seven days. Complex **3** however precipitated as a fine white powder when KPF_6 was added to the solution containing $Zn(OAc)_2$, HL^1 and triethylamine.

The IR spectra of complexes **1**–**3** show absorption bands at ≈1610 and ≈1580 cm^{-1} for $\nu_{C=N}$ and ν_{C-C} respectively and bands at 1555 and 1440 cm^{-1} are assigned to ν_{asym}(OAc) and ν_{sym}(OAc) indicating the presence of a bridging acetate anion.[19] A further single band at 1087 cm^{-1} in the spectrum of complex **1** is assigned to the ClO_4^- anions and a band at 880 cm^{-1} in the spectrum of complex **3** is assigned to the PF_6^- anions.

The structure of $[Zn_2L^1(OAc)](ClO_4)_2\cdot$MeOH (**1a**) is depicted in Fig. 1 and that of $[Zn_2L^1(OAc)](BPh_4)_2\cdot 6H_2O$ (**2a**) in Fig. 2 with selected bond lengths and angles given in the captions to the figures. In addition to the complex cation the asymmetric

Table 1 Crystal data and structure refinement for $[Zn_2L^1(OAc)](ClO_4)_2\cdot CH_3OH$ (**1a**), $[Zn_2L^1(OAc)](BPh_4)_2\cdot 6H_2O$ (**2a**), $[Zn_2L^2(OAc)](PF_6)_2$ (**4a**) and $[Zn_2L^3(OAc)]\cdot 2.5H_2O\cdot 1.5CH_3OH$ (**8a**)

	1a	**2a**	**4a**	**8a**
Formula	$C_{30}H_{36}Cl_2N_6O_{12}Zn_2$	$C_{77}H_{84}B_2N_6O_9Zn_2$	$C_{30}H_{34}F_{12}N_6O_3P_2Zn_2$	$C_{65}H_{86}N_8O_{18}Zn_4$
M	874.29	1389.86	947.31	1528.97
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	11.015(2)	14.4827(13)	9.4039(8)	20.849(5)
b/Å	12.411(2)	21.1339(18)	10.4375(10)	19.961(5)
c/Å	14.351(3)	25.765(2)	37.485(4)	18.994(5)
α/°	88.651(4)°	90	90	90
β/°	77.012(4)°	90.000(2)	79.794(2)	90.000(4)
γ/°	68.031(4)°	90	90	90
U/Å^3	1772.2(6)	7886.1(12)	3666.4(6)	7935(3)
Z	2	4	4	4
T/K	150(2)	150(2)	150(2)	150(2)
μ/mm^{-1}	1.574	1.327	1.499	1.259
Reflections collected	11825	49871	22986	44661
Unique reflections, R_{int}	8113, 0.0354	18829, [0.1676]	8582, [0.1273]	19085, [0.1402]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0474$, $wR2 = 0.1272$	$R_1 = 0.0858$, $wR2 = 0.2183$	$R_1 = 0.0803$, $wR2 = 0.1651$	$R_1 = 0.0927$, $wR2 = 0.2453$
R indices (all data)	$R_1 = 0.0658$, $wR2 = 0.1374$	$R_1 = 0.1916$, $wR2 = 0.2611$	$R_1 = 0.2725$, $wR2 = 0.3120$	$R_1 = 0.0927$, $wR2 = 0.2453$
Largest diff. peak and hole/e Å^3	1.096 and −0.734	1.843 and −0.680	1.630 and −0.613	1.643 and −0.599

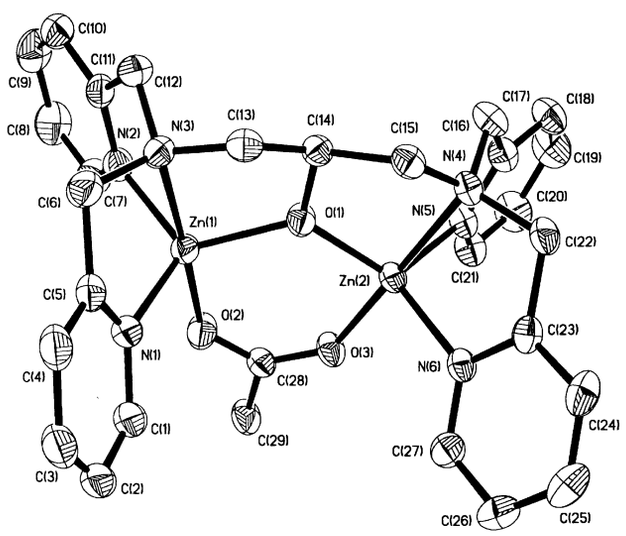


Fig. 1 ORTEP drawing of the molecular structure of the cation from **1a**, $[Zn_2L^1(OAc)]^{2+}$. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the zinc(II) atoms: Zn(1)–O(1), 1.960(2); Zn(1)–O(2), 1.987(2); Zn(1)–N(1), 2.071(3); Zn(1)–N(2), 2.050(3); Zn(1)–N(3), 2.241(3); Zn(2)–O(1), 1.943(2); Zn(2)–O(3), 1.995(2); Zn(2)–N(4), 2.248(3); Zn(2)–N(5), 2.057(3); Zn(2)–N(6), 2.042(3); Zn(1) ··· Zn(2), 3.4439(7) Å. N(3)–Zn(1)–O(2), 177.39(10); O(1)–Zn(1)–N(2), 117.84(11); N(2)–Zn(1)–N(1), 120.23(11); N(1)–Zn(1)–O(1), 112.92(10); Zn(1)–O(1)–Zn(2), 123.83(12); O(3)–Zn(2)–N(4), 178.78(10); O(1)–Zn(2)–N(5), 121.88(11); N(5)–Zn(2)–N(6), 110.23(11); O(1)–Zn(2)–N(6), 118.30(10)°.

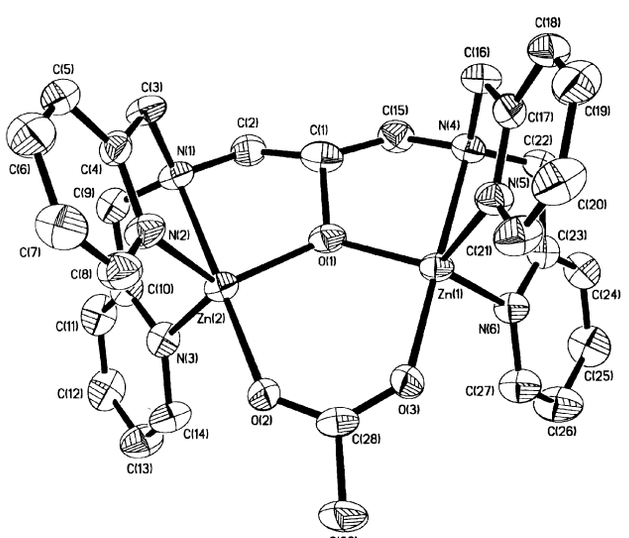


Fig. 2 ORTEP drawing of the molecular structure of the cation from **2a**, $[Zn_2L^1(OAc)]^{2+}$. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the zinc(II) atoms: Zn(1)–O(1), 1.959(4); Zn(1)–O(3), 2.011(4); Zn(1)–N(41), 2.250(5); Zn(1)–N(5), 2.059(5); Zn(1)–N(6), 2.049(5); Zn(2)–O(1), 1.962(4); Zn(2)–O(3), 2.013(4); Zn(2)–N(1), 2.247(5); Zn(2)–N(2), 2.044(5); Zn(2)–N(6), 2.046(5); Zn(1) ··· Zn(2), 3.4541(10) Å. N(4)–Zn(1)–O(3), 179.37(18); O(1)–Zn(1)–N(6), 113.43(18); N(6)–Zn(1)–N(5), 117.0(2); N(5)–Zn(1)–O(1), 120.87(19); Zn(1)–O(1)–Zn(2), 123.49(18); O(2)–Zn(2)–N(1), 179.37(18); O(1)–Zn(2)–N(2), 120.94(19); N(2)–Zn(2)–N(3), 116.9(2); O(1)–Zn(2)–N(3), 113.66(18)°.

unit for **1a** contains two perchlorate anions, one of which is disordered with an occupancy of 54.1 : 45.9%, and a disordered methanol molecule with an occupancy of 60.8 : 39.2% and the asymmetric unit for **2a** contains the complex cation, two tetraphenylborate anions, and six disordered water molecules.

In both complexes the zinc atoms are 5-coordinate with N_3O_2 donor sets derived from a bridging acetato-O atom, a bridging alkoxo-O atom, two pyridyl-N atoms and a tertiary amino-N atom. The coordination geometry is bipyramidal (*tbp*) and this is reflected in the index of trigonality, τ, which averages 0.97 for the two complexes [$\tau = 0$ for a perfect square pyramidal geometry (*sp*) and 1 for a perfect trigonal bipyramidal geometry].[20] At each zinc atom a tertiary amino-N atom and a bridging acetato-O atom serve as the axial donors with the pyridyl-N atoms and bridging alkoxo-O atom providing the equatorial donor set. The average deviation of the metals from the equatorial planes is 0.134 Å in **1a** and O.129 Å in **2a**, both in the direction of the O-donors of the acetato bridge, and the angle between the planes is 34.5 and 33.0° respectively.

The Zn–O distances for the bridging alkoxo interactions indicate that these bridges are close to symmetric [Zn(1)–O(1), 1.96; Zn(2)–O(1), 1.94 Å] in complex **1a** and symmetric [Zn(1)–O(1), 1.96; Zn(2)–O(1), 1.96 Å] in complex **2a**, and the bridging angle Zn(1)–O(1)–Zn(2) averages 123.7°. Similarly the Zn–O distances for the bridging acetato interactions indicate a high degree of symmetry [Zn(1)–O(2), 1.99; Zn(2)–O(3), 2.00 Å in complex **1a** and Zn(1)–O(3), 2.011; Zn(2)–O(2), 2.01 Å in complex **2a**]. The intermetallic separations are 3.44 (complex **1a**) and 3.45 Å (complex **2a**). The stoichiometry of complex **3** together with mass spectral evidence [m/z = 789 (100%), $[Zn_2L^1(OAc)PF_6]^+$] suggests that complex **3** will have the same cationic core structure as complexes **1** and **2**.

The coordination geometry observed in these complexes is similar to that found in the dinuclear unit of phospholipase C

in which two zinc atoms are bridged by an O atom from either a hydroxide anion or a water molecule, and through the bidentate carboxylate function of Asp122 resulting in an intermetallic separation of 3.3 Å.[21] This similarity suggests that complexes **1**–**3** could be active towards phosphate ester substrates, however in the light of recent work with related Ni(II) and Cu(II) complexes[13] it is likely that the absence of metal bound nucleophiles would lead to a diminished reactivity. In an attempt to provide complexes with metal bound water molecules or hydroxide ions pro-ligand HL^1 was reacted with Zn(II) salts of weakly or non-coordinating anions such as ClO_4^- and BF_4^- but no isolable complexes were obtained. Furthermore, attempts to isolate a discrete complex from the reaction of HL^1 with $ZnCl_2$ have not succeeded.

Complexes derived from pro-ligand HL^2

Dinuclear complexes having the general formula $[Zn_2L^2(OAc)](X)_2{\cdot}n$(solvent) where X = PF_6^- (**4**), ClO_4^- (**5**), or BPh_4^- (**6**) have been synthesised by an analogous route to that described for complexes of HL^1. Complexes **4a** and **5** crystallise as colourless blocks and complex **6** precipitated as an off-white powder on addition of $NaBPh_4$ to the reaction solution.

The IR spectra of complexes **4**–**6** show an absorption band in the range 1607–1613 cm^{-1} for $\nu_{C=N}$ and further bands at ≈1562 and ≈1440 cm^{-1} are assigned to ν_{asym}(OAc) and ν_{sym}(OAc) again indicating the presence of a bridging acetate anion.[19] FAB MS of all three complexes gave a peak for the species $[Zn_2L^2(OAc)(X)]^+$ corresponding to the loss of an anion from the molecule [*m*/*z* = 803 (37%), X = PF_6^-; 757 (35%), X = ClO_4^-; 978 (52%), X = BPh_4^-], suggesting that the core structure for each compound is similar.

The crystal structure of complex **4a**, $[Zn_2L^2(OAc)](PF_6)_2$, was solved and the complex cation is depicted in Fig. 3 with selected

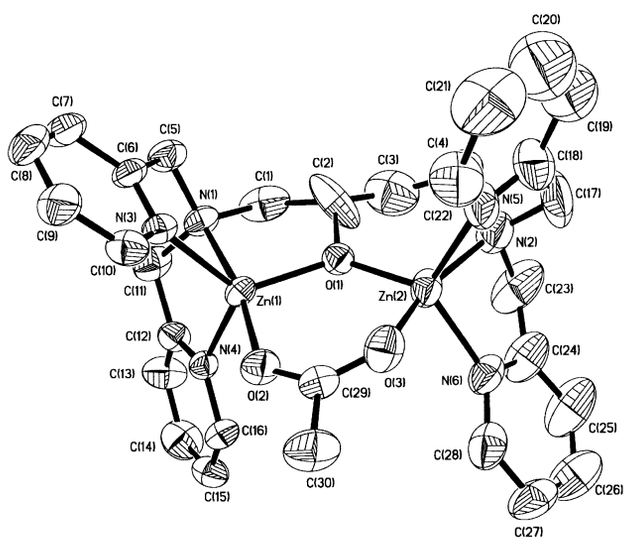


Fig. 3 ORTEP drawing of the molecular structure of the cation from **4a**, $[Zn_2L^2(OAc)]^{2+}$. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the zinc(II) atoms: Zn(1)–O(1), 1.967(4); Zn(1)–O(2), 2.001(4); Zn(1)–N(1), 2.192(5); Zn(1)–N(3), 2.074(5); Zn(1)–N(4), 2.071(5); Zn(2)–O(1), 1.937(4); Zn(2)–O(3), 2.029(5); Zn(2)–N(2), 2.182(7); Zn(2)–N(5), 2.075(6); Zn(2)–N(6), 2.076(6); Zn(1) ··· Zn(2), 3.3792(11) Å. N(1)–Zn(1)–O(2), 169.8(2); O(1)–Zn(1)–N(4), 110.72(19); N(4)–Zn(1)–N(3), 117.2 (2); N(3)–Zn(1)–O(1), 126.55(19); Zn(1)–O(1)–Zn(2), 119.9(2); O(3)–Zn(2)–N(2), 164.3(2); O(1)–Zn(2)–N(5), 117.7(2); N(5)–Zn(2)–N(6), 119.0(2); O(1)–Zn(2)–N(6), 119.7(2)°.

bond lengths and angles given in the caption to the figure. In addition to the complex cation the asymmetric unit contains two PF_6^- anions which are disordered with occupancies of 40.1 : 59.9 and 9.8 : 90.2%.

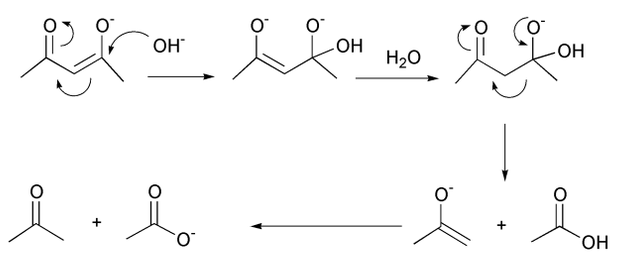
As in the complexes of HL^1 the zinc atoms are 5-coordinate with N_3O_2 donor sets derived from a bridging acetato-O atom, a bridging alkoxo-O atom, two pyridyl-N atoms and a tertiary amino-N atom. The coordination geometries are irregular *tbp* [average $\tau = 0.73$] and this distortion is induced by the flexibility introduced through the presence of an additional C-atom in the alkoxide spacer. The distortion is further illustrated by apical angles at the metal centres of 169.8 [O(2)–Zn(1)–N(1)] and 164.3° [O(3)–Zn(2)–N(2)].

A tertiary amino-N atom and a bridging acetato-O atom serve as the axial donors at each zinc atom with the pyridyl-N atoms and bridging alkoxo-O atom providing the equatorial donor set. The deviation of the metals from the equatorial planes is 0.10 at Zn(1) and 0.08 Å at Zn(2) towards the bridging acetato-O atoms and the angle between the planes is 46.2°.

The Zn–O distances for the bridging alkoxo interactions are 1.967(4) [Zn(1)–O(1)] and 1.937(4) Å [Zn(2)–O(1)] and reflect the asymmetry in the ligand backbone. The associated bridging angle [Zn(1)–O(1)–Zn(2)] is 119.9°, less than that found in **1a** and **2a**. The Zn–acetato interactions are 2.00 [Zn(1)–O(2)] and 2.03 Å [Zn(2)–O(3)] showing a slight deviation from the symmetry noted for the acetate bridges in **1a** and **2a**. The intermetallic separation of 3.38 Å is slightly shorter than those observed in **1a** and **2a**.

Complexes derived from pro-ligand H_3L^3

The complexes $[Zn_2L^3(OAc)]{\cdot}n$(solvent) (**7**, **8**) were recovered from the reactions of pro-ligand H_3L^3 with either $Zn(OAc)_2$ (**7**) or $Zn(acac)_2$ (**8**: acacH = pentane-2,4-dione). In both cases colourless crystals were obtained by slow evaporation of the reaction solution but only those from the latter reaction were suitable for X-ray analysis. No discrete complexes were isolated from reactions of H_3L^3 with Zn salts of non-coordinating anions. The isolation of an acetato-containing complex from the reaction involving $Zn(acac)_2$ was unexpected and it is proposed that the long crystallisation time of four weeks has induced the decomposition of the pentane-2,4-dionate into acetate anions and 2-propanone. A suggested reaction pathway is shown in Scheme 1 where the attacking nucleophile, OH^-, could be free or metal bound as in "$LZnOH^-$".



Scheme 1 Proposed pathway for the slow decomposition of pentane-2,4-dione into acetic acid and 2-propanone.

The crystal structure of $[Zn_2L^3(OAc)]{\cdot}2.5H_2O{\cdot}1.5CH_3OH$ (**8a**) was solved and the molecular structure of the two molecules of $[Zn_2L^3(OAc)]$ (molecule I and molecule II) are depicted in Fig. 4 with selected bond lengths and angles given in the caption to the figure. The asymmetric unit comprises two molecules of the complex, three molecules of methanol and five water molecules- all bar one of which are disordered with occupancies of 44.5 : 55.5%.

The molecules have (μ-alkoxo)(μ-acetato) cores and each 5-coordinate zinc atom has N_2O_3 donor sets derived from a bridging acetato-O atom, a bridging alkoxo-O atom, a pyridyl-N atom, a phenolato-O atom and a tertiary amino-N atom. A tertiary amino-N atom and a bridging acetato-O atom serve as the axial donors in the *tbp* geometry and the average τ value is 0.79 indicating a distortion away from ideal *tbp* geometry which lies closer to that found in **4a** ($\tau = 0.73$) than in **1a** and **2a** (average $\tau = 0.97$).

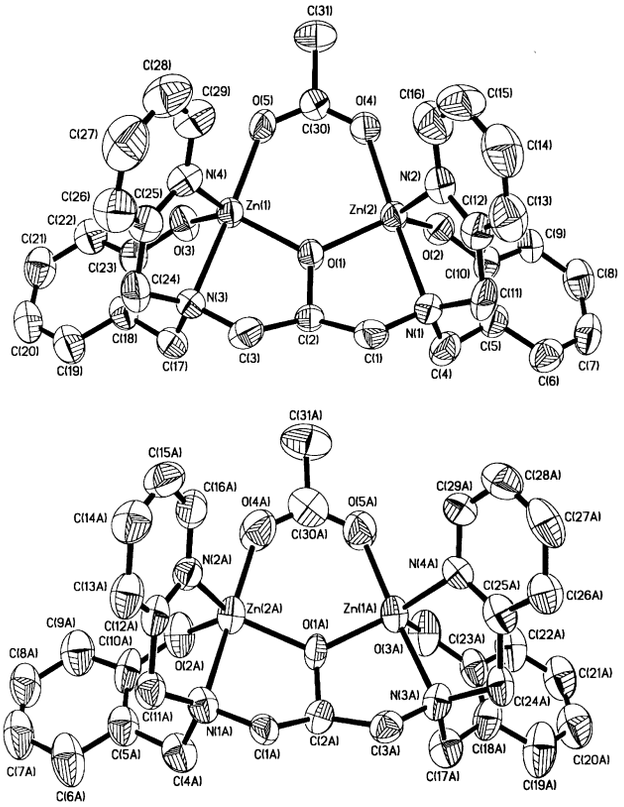


Fig. 4 ORTEP drawings of the molecular structures of $[Zn_2L^3(OAc)]$—molecule I and molecule II—from **8a**. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the zinc(II) atoms for molecule I: Zn(1)–O(1), 1.971(6); Zn(1)–O(3), 1.955(7); Zn(1)–O(5), 2.047(7); Zn(1)–N(3), 2.219(8); Zn(1)–N(4), 2.111(8); Zn(2)–O(1), 1.972(6); Zn(2)–O(2), 1.960(7); Zn(2)–O(4), 2.051(7); Zn(2)–N(1), 2.219(8); Zn(2)–N(2), 2.112(9); Zn(1) ··· Zn(2), 3.5256(17) Å. N(3)–Zn(1)–O(5), 171.1(3); O(1)–Zn(1)–N(4), 112.0(3); N(4)–Zn(1)–O(3), 121.8 (3); O(3)–Zn(1)–O(1), 123.3(3); Zn(1)–O(1)–Zn(2), 126.8(3); O(4)–Zn(2)–N(1), 170.4(3); O(1)–Zn(2)–N(2), 111.8(3); N(2)–Zn(2)–O(2), 121.8(3); O(1)–Zn(2)–O(2), 123.5(3)°. For molecule II: Zn(1A)–O(1A), 1.967(6); Zn(1A)–O(3A), 1.989(8); Zn(1A)–O(5A), 2.040(8); Zn(1A)–N(3A), 2.209(8); Zn(1A)–N(4A), 2.117(8); Zn(2A)–O(1A), 1.966(6); Zn(2A)–O(2A), 1.966(7); Zn(2A)–O(4A), 2.035(9); Zn(2A)–N(1A), 2.204(8); Zn(2A)–N(2A), 2.116(8); Zn(1A) ··· Zn(2A), 3.5432(17) Å. N(3A)–Zn(1A)–O(5A), 170.0(3); O(1A)–Zn(1A)–N(4A), 116.5(3); N(4A)–Zn(1A)–O(3A), 119.2 (3); O(3A)–Zn(1A)–O(1A), 122.1(3); Zn(1A)–O(1A)–Zn(2A), 128.5(3); O(4A)–Zn(2A)–N(1A), 170.4(3); O(1A)–Zn(2A)–N(2A), 116.8(3); N(2A)–Zn(2A)–O(2A), 118.7(3); O(1A)–Zn(2A)–O(2A), 122.1(3)°

A pyridyl-N atom, a phenolato-O atom and bridging alkoxo-O atom provide the equatorial donor set and the deviations of the metals from the equatorial planes average 0.075 in molecule I and 0.066 Å in molecule II. The metals are displaced towards the bridging acetato-O atoms and the angle between the planes are 41.7 and 41.1° respectively. The average deviation is considerably less than that observed for complexes **1a** and **2a** and is probably due to the presence of the 6-membered rings in the complex (Fig. 5), arising from coordination of the phenolato-pendant arms, allowing the complex to relax. This is reflected in the increased Zn(1)–O(1)–Zn(2) angle of 126.8° [Zn(1A)–O(1A)–Zn(2A), 128.5°] and an increased Zn ··· Zn separation averaging 3.53 Å. The Zn–O distances for the bridging alkoxo interactions are all close to 1.97 Å indicating the symmetric nature of the bridge; the Zn-acetato interactions also provide symmetric bridges, [Zn(1)–O(5)], [Zn(2)–O(4)] 2.05 and [Zn(1A)–O(5A)], [Zn(2A)–O(4A)] 2.05 Å.

It was noted above that the coordination geometry observed in these complexes is similar to that found in the dinuclear unit of phospholipase C and so the complexes may be regarded as structural analogues for this dinuclear unit. The functionality

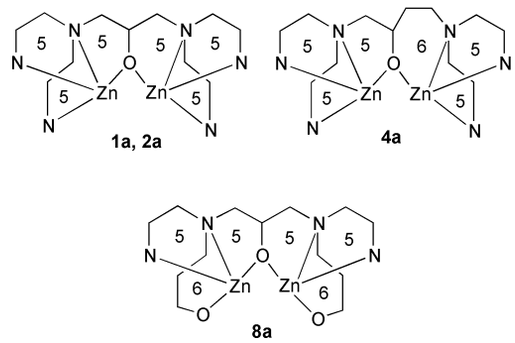


Fig. 5 Schematic representation of the complex skeletons arising in complexes **1a**, **2a**, **4a** and **8a**.

of model complexes for zinc enzymes is usually governed by the presence of metal bound nucleophiles and so it is necessary to draw attention to the absence of such species from the structural analogues presented here.[22,23]

The atomic frameworks of complexes **1a** and **2a** (Fig. 5) are dominated by the formation of 5-membered chelate rings. It is likely that the rigidity imposed by this restricts the geometry at the metal atoms to an almost ideal *tbp* arrangement (τ_{mean} = 0.97) and makes it very difficult for the metal atoms to distort this geometry in order to expand their coordination spheres. Ligands which form 5-membered chelate rings have been proposed to have a greater donor ability than those which form 6-membered rings with the same donor set.[24–26] As a consequence of these two effects there are no solvent molecules attached to the metal centres. Introduction of asymmetry into the ligand spine through an additional C-atom as in complex **4a** results in the introduction of a 6-membered ring in a bridging position. This affords a distortion from ideal geometry as evidenced by the τ factor of 0.73. No solvent molecules are coordinated to the metals and so the increased ligand flexibility permitted by the 6-membered bridging chelate, which also has a weaker donor ability, is insufficient to allow the metal atoms to expand their coordination spheres. When two of the pyridinyl pendant arms are replaced by two phenolic pendant arms then two 6-membered rings are introduced (complex **8a**). These occupy peripheral rather than bridging positions and so increase the flexibility of the molecule (τ = 0.79) but the introduction of additional oxygen donors (as $-O^-$), to produce a neutral core rather than a cationic one, probably offsets this by increasing the donor power of the ligand over that of the tetrapyridinyl analogue. Again no solvent molecules are coordinated to the metals. In order to facilitate solvent molecule incorporation, as a prerequisite for hydrolytic activity, it is suggested that the number of 6-membered ring chelates within the complex should be increased and that a phenolate group be introduced into the ligand spine as it would provide a weaker donor atom than the alkoxo-bridge.[5,6]

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