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Synthesis and structure of mononuclear and binuclear zinc(II) compartmental macrocyclic complexes

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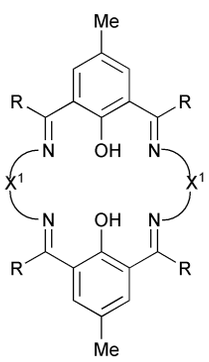
The structures of four neutral binuclear Zn^{II} complexes of the Schiff-base macrocycles formed by the [2+2] template condensation of 2,6-diformyl-4-methylphenol with 1,2-diaminoethane: [H_2L^1], 1,3-diaminopropane: [H_2L^2], 1,4-diaminobutane: [H_2L^3] and 2,6-diacetyl-4-methylphenol with 1,2-diaminoethane: [H_2L^4] have been determined. The complexes [$Zn_2(L^1)(OAc)_2$]·2$CHCl_3$, [$Zn_2(L^2)(OAc)_2$]·2$CHCl_3$ and [$Zn_2(L^4)Cl_2$] each contain two five coordinate Zn^{II} centres with each metal ion bound to the N_2O_2 donor set of the macrocyclic ligand and to an anion molecule. Two different coordination environments are observed in [$Zn_2(L^3)$(μ-OAc)(OAc)]·$CHCl_3$ which contains both a five- and a six-coordinate Zn^{II} centre, with one acetate bridging two metal ions and a monodentate acetate bound to the six-coordinate Zn^{II} ion. Significantly, the reaction of pre-formed macrocyclic ligands [H_4L^2]$(PF_6)_2$ and [H_4L^4]$(PF_6)_2$ with $Zn(OAc)_2$·2H_2O affords [$Zn_2(L^2)$(μ-OAc)](PF_6)·MeCN and [$Zn(H_2L^4)$(MeCN)]$(PF_6)_2$, respectively. The former shows two five-coordinate Zn^{II} centres in which an acetate bridges both metal ions. In the latter complex the macrocyclic ligand binds only one five-coordinate Zn^{II} ion with a molecule of MeCN bound at an apical position.

Introduction

In the early 1970s, Robson and Pilkington first reported the template synthesis of a compartmental macrocyclic ligand based upon the 2 + 2 condensation of 1,3-diaminopropane with 2,6-diformyl-4-methylphenol in the presence of a transition metal salt.[1] This new ligand contained two bisiminophenol moieties and was capable of binding two metal ions in close proximity. Since then, a large body of work has been reported on this and related macrocyclic systems.[2] The homo- and hetero-bimetallic complexes of these ligands[2] and their thiophenol analogues[3] have undergone extensive electrochemical and magnetochemical studies, often with the aim of modelling active sites of metalloenzymes and mimicking their activity by binding and activating small molecules.[4] However, apart from a few examples, the study of binuclear Zn^{II} complexes has been neglected despite their importance in the active sites of a number of biological systems, including phospholipase c and leucine aminopeptidase.[5]

The structures of the three binuclear Zn^{II} complexes of $[L^2]^{2-}$ (Scheme 1) reported previously represent the only structurally characterised examples of Zn^{II} complexes of a ligand derived from a non-functionalised diamine, namely 1,3-diaminopropane.[6] These complexes were synthesised by transmetallation of the disodium salt of the ligand with $Zn(ClO_4)_2$·6H_2O or $Zn(NO_3)_2$·6H_2O. The structure of the perchlorate complex, [$Zn_2(L^2)(H_2O)_2$]$(ClO_4)_2$, reveals a pair of independent binuclear Zn^{II} complexes (molecules 1 and 2), the main difference being the length of the Zn–$OClO_3$ interaction. In molecule 1, the ClO_4^- ion is considered to be bound to the Zn^{II} to give a distorted octahedral geometry [N_2O_2(ligand), O(H_2O) and O($OClO_3$)]. In molecule 2, however, the ClO_4^- is more remote and each Zn^{II} exhibits a distorted square pyramidal geometry [N_2O_2(ligand), O(H_2O)]. The observed Zn ··· Zn distances are 3.166(4) and 3.177(4) Å, respectively. The corresponding azide complex [$Zn_2(L^2)(N_3)_2$] was prepared by transmetallation of the disodium salt of the ligand with $Zn(OAc)_2$·2H_2O followed by anion metathesis with NaN_3.[6] This complex contains two Zn^{II} ions with distorted square pyramidal geometry (N_2O_2 donor set from ligand and N donor from N_3) with a Zn ··· Zn distance of 3.333(3) Å. The structure of a similar bimetallic complex [Zn_2(L)(H_2O)$_2$]$(ClO_4)_2$ (where L is derived from 2,6-diformyl-4-chlorophenol) has also been reported.[7] The structural features of [Zn_2(L)(H_2O)$_2$]$(ClO_4)_2$ are very similar to those observed[6] previously in [$Zn_2(L^2)(H_2O)_2$]$(ClO_4)_2$, and both complexes have been used as building blocks for the construction of molecular ladders.[8] Recently, the first structure of a bimetallic Zn^{II} complex which contains a shorter diamine bridge (*trans*-(1*R*,2*R*)-cyclohexanediamine) has been reported.[9] This compound was obtained as the rearrangement product of the reaction of the preformed [3 + 3] macrocyclic ligand with $Zn(OAc)_2$·H_2O under reflux conditions. The literature also contains three examples of tetranuclear Zn^{II} complexes of ligands synthesised by the reaction of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol[10] and 1,11-diamino-3,6,9-trioxaundecane.[11] These complexes contain examples of four-, five- and six-coordinate Zn^{II} centres where, in the absence of ligand field stabilisation energy, the coordination at Zn^{II} is determined by subtle steric and electronic effects. Thus, despite the large body of work on the Robson ligand system, the



H_2L^1 where $X^1 = (CH_2)_2$ and R = H
H_2L^2 where $X^1 = (CH_2)_3$ and R = H
H_2L^3 where $X^1 = (CH_2)_4$ and R = H
H_2L^4 where $X^1 = (CH_2)_2$ and R = Me

Scheme 1 Ligands used in this study.

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ligands $[H_4L^1]^{2+}$ and $[H_4L^3]^{2+}$, with the smallest and largest cavity size of the series, respectively, have few structurally-characterised examples, none of which are complexes with Zn^{II}.

We describe herein the effects on the observed compartmental Zn^{II} complexes by simple alteration of the diimine linker and thus variation of the hole-size of the resultant macrocycle. We report the structures of four binuclear Zn^{II} complexes formed by template condensation of Zn^{II} with 2,6-diformyl-4-methylphenol (or 2,6-diacetyl-4-methylphenol) and a series of diamines. To our knowledge, this paper includes the first example of a crystallographically characterised binuclear Zn^{II} complex of the tetramethylene-linked system.

We have reported previously the synthesis and characterisation of a series of metal-free, protonated Robson-type macrocycles.[12] Our interest in such systems is derived from their potential as metal cation extractants.[13] Significantly, we find that metal insertion reactions using pre-formed ligands afford different complex products compared to direct metal-template condensation reactions. We report a mononuclear and a binuclear complex formed by the reaction of $Zn(OAc)_2 \cdot 2H_2O$ with two pre-formed protonated macrocyclic ligands $[H_4L^4](PF_6)_2$ and $[H_4L^2](PF_6)_2$, respectively.

Results and discussion

Template syntheses of 1, 2 and 3

The complexes $[Zn_2(L^1)(OAc)_2]$ **1**, $[Zn_2(L^2)(OAc)_2]$ **2** and $[Zn_2(L^3)(\mu\text{-OAc})(OAc)]$ **3**, were synthesised by the addition of the appropriate diamine to a mixture of $Zn(OAc)_2 \cdot 2H_2O$ and 2,6-diformyl-4-methylphenol in $CHCl_3$–MeOH solution. The formation of the required 2 + 2 macrocycles was confirmed by FAB mass spectrometry which showed peaks for $[M - (OAc)]^+$ and $[M - 2(OAc)]^+$ corresponding to the loss of one and both acetates from the complex, respectively. The IR spectra of **1**, **2** and **3** all show an absorption near 1635 cm^{-1} corresponding to the C=N stretching vibration. No absorptions corresponding to the carbonyl or amine moieties from unreacted starting materials were observed. The absorptions corresponding to asymmetric and symmetric stretching of the acetate groups in **2** were observed at 1609 and 1411 cm^{-1}, respectively,[14] and, additionally these bands may also be indicative of a monodentate binding of the acetate. The broad absorptions associated with the stretching vibration of the acetate in **3** suggested the acetate bonding was more complicated. The ^1H NMR spectra of **1**, **2** and **3** each contain only one imine proton resonance and only one methyl proton resonance for the acetate group is indicative of symmetry in the system in solution. In the case of **2** and **3**, the signals for the protons found on the trimethylene and tetramethylene linkers were not fully resolved and gave only broad signals due probably to fluxional twisting of the linker in solution. X-Ray crystallographic studies were undertaken to determine the conformation of the ligands and to confirm the bonding modes of the acetate ions.

The molecular structure of **1**·$2CHCl_3$ is shown in Fig. 1 with selected bond lengths and bond angles in Table 1. The binuclear complex lies across a crystallographic inversion centre. The Zn^{II} ions are 3.183(1) Å apart and are disposed in an *anti* arrangement, and are displaced by 0.772 Å in opposite directions from the plane of the donor atoms. Each metal ion has distorted square pyramidal geometry supported by an N_2O_3 donor set, *i.e.* two bridging phenoxy oxygens [Zn(1)–O(1) and Zn(1)–O(1^i) 2.010(3), 2.035(3) Å, i = $-x$, $-y+1$, $-z$], two imine nitrogens [Zn(1)–N(1) and Zn(1)–N(2) 2.058(3), 2.046(3) Å] and a monodentate acetate oxygen, [Zn(1)–O(2) 1.953(3) Å]. The Zn ··· Zn intermetallic distance, bond distances and displacement from the N_2O_2 donor set are very similar to those found in the binuclear Zn^{II} complexes of the *trans*-(1*R*,2*R*)-cyclohexanediamine bridged ligand.[9] As far as we are aware there are no previously reported structures of binuclear Zn^{II} complexes of the ligand H_2L^1.

Table 1 Selected bond lengths [Å] and angles [°] for $[Zn_2(L^1)(OAc)_2] \cdot 2CHCl_3$, **1**·$2CHCl_3$

Zn(1)–O(1)	2.010(3)	Zn(1)–N(1)	2.058(3)
Zn(1)–O(2)	1.953(3)	Zn(1)–N(2)	2.046(3)
Zn(1)–O(1^i)	2.035(3)	Zn(1) ··· Zn(1^i)	3.183(1)
O(1)–Zn(1)–O(2)	100.41(12)	N(1)–Zn(1)–N(2)	82.49(12)
O(1^i)–Zn(1)–O(2)	104.71(13)	C(8)–N(1)–Zn(1)	126.0(3)
O(1)–Zn(1)–O(1^i)	76.22(11)	C(9)–N(1)–Zn(1)	112.2(2)
O(1)–Zn(1)–N(2)	140.43(12)	C(11)–N(2)–Zn(1)	127.2(3)
O(2)–Zn(1)–N(2)	117.70(12)	C(10)–N(2)–Zn(1)	109.6(2)
O(1^i)–Zn(1)–N(2)	83.79(11)	C(1)–O(1)–Zn(1)	129.0(2)
N(1)–Zn(1)–O(2)	123.98(12)	C(1)–O(1)–Zn(1^i)	126.5(2)
O(1)–Zn(1)–N(1)	84.91(12)	C(12)–O(2)–Zn(1)	113.2(2)
O(1^i)–Zn(1)–N(1)	130.23(12)	Zn(1)–O(1)–Zn(1^i)	103.78(11)

Symmetry code: i $-x$, $-y+1$, $-z$.

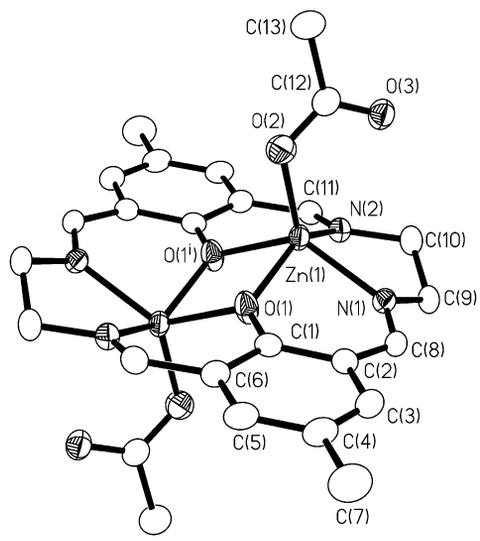

Fig. 1 An ORTEP view of **1**·$2CHCl_3$ with 50% probability ellipsoids. H-atoms and chloroform solvent molecules have been omitted for clarity. Symmetry operation used to generate equivalent atoms: $-x$, $-y+1$, $-z$.

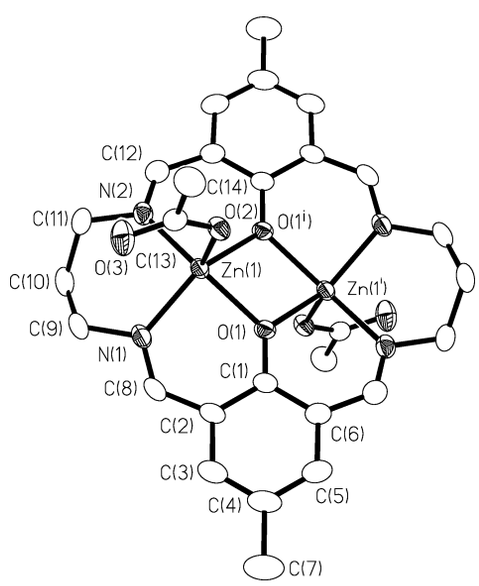

Fig. 2 An ORTEP view of **2**·$2CHCl_3$ with 50% probability ellipsoids. The solvent molecules have been omitted for clarity. Symmetry operation used to generate equivalent atoms: $-x$, $-y$, $-z+2$.

The molecular structure of **2**·$2CHCl_3$ is shown in Fig. 2 and selected bond lengths and bond angles are given in Table 2. The

Table 2 Selected bond lengths [Å] and angles [°] for $[Zn_2(L^2)(OAc)_2]\cdot 2CHCl_3$, $\mathbf{2}\cdot 2CHCl_3$

Zn(1)–O(1)	2.087(2)	Zn(1)–N(1)	2.076(3)
Zn(1)–O(2)	1.984(2)	Zn(1)–N(2)	2.096(3)
Zn(1)–O(1^i)	2.081(2)	Zn(1) ··· Zn(1^i)	3.131(1)
O(1)–Zn(1)–O(2)	101.57(10)	O(1^i)–Zn(1)–N(2)	87.16(10)
O(1)–Zn(1)–O(1^i)	74.74(10)	O(2)–Zn(1)–N(1)	116.53(10)
O(1)–Zn(1)–N(1)	87.70(11)	O(2)–Zn(1)–N(2)	104.44(10)
O(1)–Zn(1)–N(2)	149.88(10)	N(1)–Zn(1)–N(2)	94.02(12)
O(2)–Zn(1)–O(1^i)	97.07(9)	Zn(1)–O(1)–Zn(1^i)	105.26(10)
O(1^i)–Zn(1)–N(1)	144.76(10)		

Symmetry code: i $-x, -y, -z+2$.

structure of $\mathbf{2}\cdot 2CHCl_3$ was found to be analogous to that of $\mathbf{1}\cdot 2CHCl_3$, each Zn^{II} having an analogous N_2O_3 donor set: two bridging phenoxy oxygens [Zn(1)–O(1) and Zn(1)–O(1^i) 2.087(2), 2.081(2) Å, i = $-x, -y, -z+2$], two imine nitrogens [Zn(1)–N(1) and Zn(1)–N(2) 2.076(3), 2.096(3) Å] and a monodentate acetate oxygen, [Zn(1)–O(2) 1.984(2) Å]. The Zn^{II} ions are disposed out of the plane of the donor set of the macrocycle by 0.557 Å with an intermetallic distance of 3.313(1) Å. Increasing the size of the cavity in the macrocycle decreases the mismatch between the cavity size and cationic diameter, and increases the distance between the Zn^{II} ions and decreases their displacement out of the plane of the macrocyclic ligand. The Zn ··· Zn distance and the displacement of the Zn^{II} from the N_2O_2 donor plane of the ligand, 3.333(3) and 0.532 Å, respectively, are in accord with parameters observed in $[Zn_2(L^2)(N_3)_2]$.[6]

The molecular structure of $\mathbf{3}\cdot CHCl_3$ is shown in Fig. 3 and selected bond lengths and bond angles are given in Table 3. Although changing the diamine used in the template condensation had little effect on the structure on going from the $-(CH_2)_2-$ linked to the $-(CH_2)_3-$ linked macrocycles, increasing the length of the hydrocarbon chain from $(CH_2)_3$ to $(CH_2)_4$ had a more pronounced effect. Although the complex formed is again the [2 + 2] macrocyclic product containing two Zn^{II} ions and two acetate moieties, the macrocycle adopts a twisted conformation to allow one acetate ligand to bridge the two metal centres. The intermetallic distance of 3.120(2) Å is shorter than in the $-(CH_2)_2-$ and $-(CH_2)_3-$ linked complexes and the acetate binding to Zn^{II} is also altered in the $-(CH_2)_4-$ linked product. $\mathbf{3}\cdot CHCl_3$ contains both a six- and a five-coordinate Zn^{II}, the coordination geometry of the former being distorted octahedral with an N_2O_4 donor set provided by two bridging

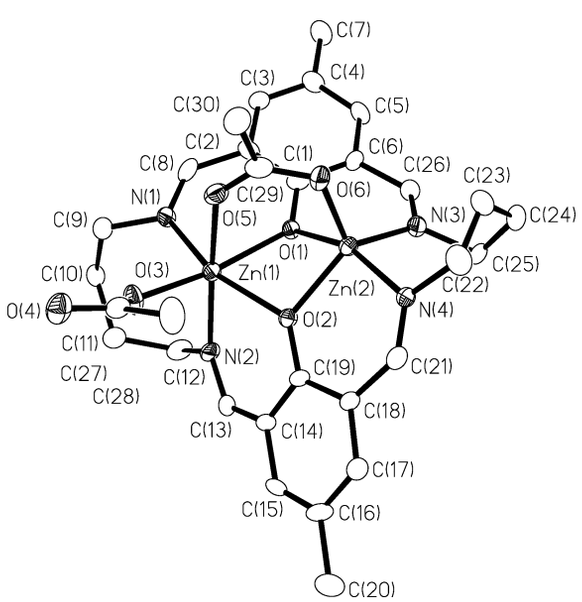

Fig. 3 An ORTEP view of $\mathbf{3}\cdot CHCl_3$ with 50% probability ellipsoids. The H atoms and the chloroform solvent molecule have been omitted for clarity.

Table 3 Selected bond lengths [Å] and angles [°] for $[Zn_2(L^3)(OAc)_2]\cdot CHCl_3$, $\mathbf{3}\cdot CHCl_3$

Zn(1) ··· Zn(2)	3.120(2)	Zn(1)–N(2)	2.112(8)
Zn(1)–O(1)	2.099(6)	Zn(2)–O(1)	2.094(6)
Zn(1)–O(2)	2.131(6)	Zn(2)–O(2)	1.988(6)
Zn(1)–O(3)	2.028(6)	Zn(2)–O(6)	1.961(6)
Zn(1)–O(5)	2.259(6)	Zn(2)–N(3)	2.025(8)
Zn(1)–N(1)	2.090(7)	Zn(2)–N(4)	2.117(7)
O(1)–Zn(1)–O(2)	73.7(2)	O(5)–Zn(1)–N(2)	167.6(3)
O(1)–Zn(1)–O(3)	166.7(3)	N(1)–Zn(1)–N(2)	98.2(3)
O(1)–Zn(1)–O(5)	82.9(2)	O(1)–Zn(2)–O(2)	76.8(2)
O(1)–Zn(1)–N(1)	86.2(3)	O(1)–Zn(2)–O(6)	100.8(3)
O(1)–Zn(1)–N(2)	102.5(3)	O(1)–Zn(2)–N(3)	85.0(3)
O(2)–Zn(1)–O(3)	104.8(3)	O(1)–Zn(2)–N(4)	160.6(3)
O(2)–Zn(1)–O(5)	88.7(2)	O(2)–Zn(2)–O(6)	109.2(3)
O(2)–Zn(1)–N(1)	159.4(3)	O(2)–Zn(2)–N(3)	131.3(3)
O(2)–Zn(1)–N(2)	82.3(3)	O(2)–Zn(2)–N(4)	87.5(3)
O(3)–Zn(1)–O(5)	83.9(3)	O(6)–Zn(2)–N(3)	118.4(3)
O(3)–Zn(1)–N(1)	95.9(3)	O(6)–Zn(2)–N(4)	95.0(3)
O(3)–Zn(1)–N(2)	90.2(3)	N(3)–Zn(2)–N(4)	97.3(3)
O(5)–Zn(1)–N(1)	93.3(3)	Zn(1)–O(1)–Zn(2)	96.2(2)
		Zn(1)–O(2)–Zn(2)	98.4(2)

phenoxy oxygens [Zn(2)–O(1) and Zn(1)–O(2) 2.094(6), 2.131(6) Å], two imine nitrogens [Zn(1)–N(1) and Zn(1)–N(2) 2.090(7), 2.112(8) Å], a monodentate acetate oxygen [Zn(1)–O(3) 2.028(6) Å] and an oxygen from a bridging acetate [Zn(1)–O(5) 2.259(6) Å]. The geometry of the five-coordinate Zn^{II} centre is very similar to that of the Zn^{II} ions found in $[Zn_2(L^1)(OAc)_2]$ and $[Zn_2(L^2)(OAc)_2]$, being distorted square pyramidal with an N_2O_3 donor set provided by two bridging phenoxy oxygens [Zn(2)–O(1) and Zn(2)–O(2) 2.094(6), 1.988(6) Å], two imine nitrogens [Zn(2)–N(3) and Zn(2)–N(4) 2.025(8), 2.117(7) Å] and an oxygen from a bridging acetate [Zn(2)–O(6) 1.961(6) Å]. Therefore, increasing the ligand ring size leads in **3** to a decrease in the Zn ··· Zn separation *via* bridging acetate coordination that is not observed in **1** or **2**.

Reaction of $[H_4L^4](PF_6)_2$ and $[H_4L^2](PF_6)_2$ with $Zn(OAc)_2\cdot 2H_2O$

In order to test different synthetic strategies to binuclear Zn^{II} complexes, we undertook a study of metal insertion into metal-free, pre-formed ligands as a comparison with more generally applicable metal-template methods of synthesis. The metal-free protonated ligands $[H_4L^4](PF_6)_2$ and $[H_4L^2](PF_6)_2$ were obtained by reaction of the appropriate dialdehyde or diketone in the presence of HBr in MeOH solution.[12] The PF_6^- salt was isolated by anion metathesis with NH_4PF_6. These ligands were both reacted with $Zn(OAc)_2\cdot 2H_2O$ and, in the case of $\mathbf{5}\cdot$MeCN, excess NaOAc.

The IR spectrum of $[Zn(H_2L^4)(MeCN)](PF_6)_2$ **4** shows an imine stretching vibration and the presence of PF_6^- counter-ions. The IR spectrum of **4** was similar to that of the starting material, $[H_4L^4](PF_6)_2$, the differences being a shift in the intense absorption at 1538 cm^{-1} in the metal-free ligand to 1559 cm^{-1} in the complex, and subtle variations in the 1250–1450 cm^{-1} region. The ^1H NMR spectrum of the crystalline material showed signals corresponding to eight unique macrocyclic proton environments. The aromatic CH signals were doublets (^4J = 1.9 Hz) as a result of mutual coupling. This asymmetry, together with the presence of a broad signal at 16.38 ppm which is also observed in $[H_4L^4](PF_6)_2$, suggested that the ligand was not fully deprotonated, and that only one metal ion has been bound. The FAB mass spectrum of the crystalline solid showed a peak corresponding to the cation $[Zn(L^4)]^+$, and a peak assignable to $[H_3L^4]^+$ was also observed. In order to confirm the stoichiometry and connectivity of the product a single-crystal X-ray structure determination was undertaken.

The molecular structure of complex **4** is shown in Fig. 4 with selected bond lengths and bond angles given in Table 4. The complex is mononuclear, but with the Zn^{II} ion disordered

Table 4 Selected bond lengths [Å] and angles [°] for $[Zn(H_2L^4)(MeCN)](PF_6)_2$, **4**

Zn(1)–O(1)	1.976(4)	Zn(2)–O(1)	1.953(7)
Zn(1)–O(2)	1.969(4)	Zn(2)–O(2)	1.833(7)
Zn(1)–N(1)	2.045(5)	Zn(2)–N(3)	2.106(8)
Zn(1)–N(2)	2.040(5)	Zn(2)–N(4)	2.272(7)
Zn(1)–N(1S)	2.040(6)		
O(1)–Zn(1)–O(2)	86.1(2)	N(1S)–Zn(1)–N(2)	104.5(2)
O(1)–Zn(1)–N(1)	86.9(2)		
O(1)–Zn(1)–N(1S)	102.8(2)	O(1)–Zn(2)–O(2)	90.6(3)
O(1)–Zn(1)–N(2)	152.6(2)	O(1)–Zn(2)–N(3)	139.1(4)
O(2)–Zn(1)–N(1)	149.7(2)	O(1)–Zn(2)–N(4)	72.3(3)
O(2)–Zn(1)–N(1S)	104.9(2)	O(2)–Zn(2)–N(3)	79.7(3)
O(2)–Zn(1)–N(2)	87.8(2)	O(2)–Zn(2)–N(4)	131.7(4)
N(1)–Zn(1)–N(1S)	105.3(2)	N(3)–Zn(2)–N(4)	84.8(3)
N(1)–Zn(1)–N(2)	85.1(2)		

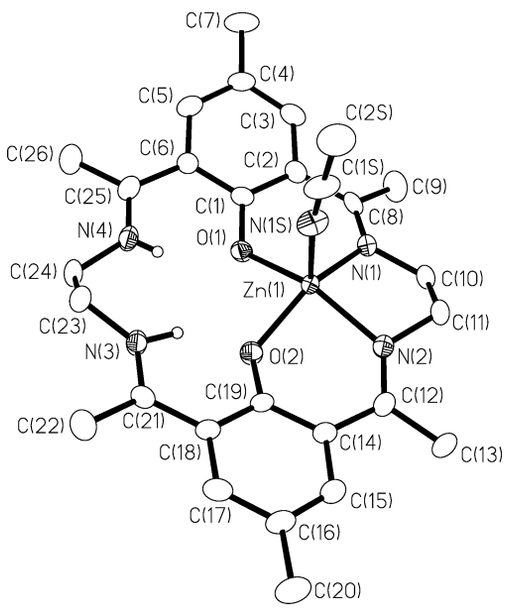

Fig. 4 An ORTEP view of the cation of **4** with 50% probability ellipsoids. The H atoms and the PF_6^- have been omitted for clarity.

unequally between the two cavities of the macrocycle: the occupancies converged at 0.899(2) for Zn(1) and 0.101(2) for Zn(2). Zn(1) adopts a square-pyramidal geometry and is bound to two imine N-donors [Zn(1)–N(1) and Zn(1)–N(2) 2.045(5), 2.040(4) Å; Zn(2)–N(3) and Zn(2)–N(4) 2.106(8), 2.272(7) Å], two phenoxy O-donors [Zn(1)–O(1) and Zn(1)–O(2) 1.976(4), 1.969(4); Zn(2)–O(1) and Zn(2)–O(2) 1.953(7), 1.833(7) Å] and the N-donor of an axially ligated MeCN molecule [Zn(1)–N(1S) 2.040(6) Å] which has a Zn(1)–N(1S)–C(1S) angle of 171.9(6)°. The axial ligand attached (presumably) to Zn(2) was not located; this is not surprising given the low site occupancy of the constituent atom(s). The macrocycle $[L^4]^{2-}$ adopts a stepped conformation, with a step height of 0.99 Å reminiscent of the solid-state conformations of $[H_4L^1]^{2+}$ and $[H_4L^4]^{2+}$.[12] The ligand is also slightly folded, with an angle between the normals to the planes of the two aromatic rings of 18.5°. There is significant twisting about the C–C bonds connecting the C=N units to the aromatic rings which may allow the optimum Zn^{II}–donor atom bond lengths. There appears to be no significant intermolecular hydrogen-bonding or π–π stacking interactions in the solid state.

It is surprising that the product from the reaction of two equivalents of $Zn(OAc)_2{\cdot}2H_2O$ with one equivalent of $[H_4L^4](PF_6)_2$ is not binuclear, especially since $[Zn(H_2L^4)(MeCN)](PF_6)_2$ did not precipitate from the reaction solution and so could have reacted further to insert the second Zn^{II} ion. We have established, however, that the synthesis of $[Zn(H_2L^4)(MeCN)](PF_6)_2$ is reproducible even when excess $Zn(OAc)_2{\cdot}2H_2O$ is used. We speculate that the mononuclear Zn^{II} complex is the kinetic product of the reaction and that the reaction conditions employed did not favour the formation of the possibly binuclear thermodynamic product. Although no crystal structure was determined, Fenton and co-workers have reported the synthesis of the binuclear Zn^{II} complex, $[Zn_2(L^1)(OAc)_2]{\cdot}0.5H_2O$ by reaction of $Zn(OAc)_2{\cdot}2H_2O$ with a pre-formed acyclic ligand H_2L in ethanolic solution, where L is the ligand formed in the reaction of 2 eq. of 2,6-diacetyl-4-methylphenol with 1 eq. of 1,2-diaminopropane.[15] It was, however, observed that this complex could also be formed by template techniques.

Reaction of $[H_4L^2](PF_6)_2$ with $Zn(OAc)_2{\cdot}2H_2O$ in MeCN affords the complex $[Zn_2(L^2)(\mu\text{-}OAc)](PF_6)$, **5**. The FAB mass spectrum of **5** is consistent with the coordination of two Zn^{II} ions within the macrocyclic ligand with peaks observed corresponding to loss of the counter-ion PF_6^- and acetate. The IR spectrum of **5** confirmed the presence of PF_6^- anion and showed the asymmetric and symmetric stretching modes of the acetate groups at 1573 and 1415 cm^{-1}, respectively. The difference between the asymmetric and symmetric stretching frequencies of the acetates is consistent with a bridging mode[14] rather than the monodentate coordination observed in $[Zn_2(L^1)(OAc)_2]$ and $[Zn_2(L^2)(OAc)_2]$. Also, the imine stretching vibration was shifted compared to that of the free ligand, to a value very similar to that found in $[Zn_2(L^1)(OAc)_2]$. A structural study was undertaken to determine the configuration of the ligand around the metal.

The molecular structure of **5**·MeCN is shown in Fig. 5 and selected bond lengths and bond angles are given in Table 5. This complex also contains two Zn^{II} ions in a distorted square pyramidal geometry provided by two bridging phenoxy oxygens [Zn(1)–O(1), Zn(1)–O(2), 2.074(3), 2.036(3) Å, and Zn(2)–O(1), Zn(2)–O(2), 2.055(3), 2.079(3) Å], two imine nitrogens [Zn(1)–N(1), Zn(1)–N(2), 2.030(4), 2.056(3) Å, and Zn(2)–N(3), Zn(2)–N(4), 2.039(4), 2.054(4) Å] and an oxygen from a bridging acetate [Zn(1)–O(3), Zn(2)–O(4) 2.011(3), 2.007(3) Å]. The distance of 3.038(1) Å between the Zn^{II} ions is 0.27 Å shorter than in the $–(CH_2)_3–$ linked complex, $[Zn_2(L^2)(OAc)_2]$, formed by the template reaction. The ligand itself is not planar as in the cases of the $–(CH_2)_2–$ and $–(CH_2)_3–$ linked templated complexes: there is a dihedral angle of 17.6° between the normals to the planes formed by the phenyl rings, with the linker carbons centres lying on opposite sides of the ligand plane.

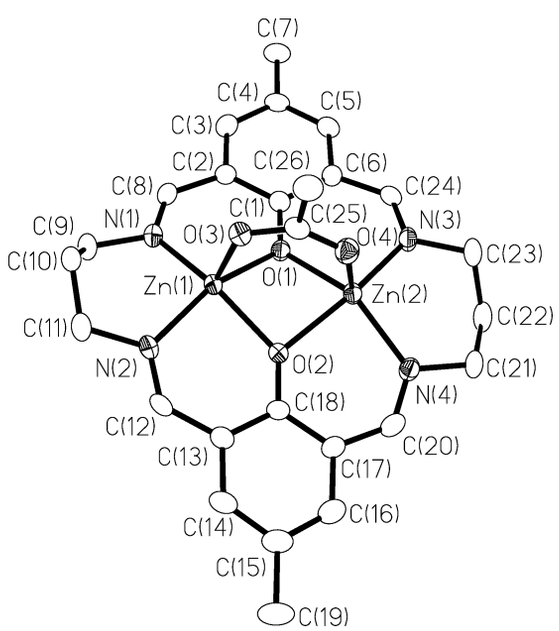

Fig. 5 An ORTEP view of **5**·MeCN with 50% probability ellipsoids. The H atoms, the PF_6^- and the acetonitrile solvent molecule have been omitted for clarity.

Table 5 Selected bond lengths [Å] and angles [°] for $[Zn_2(L^2)(OAc)](PF_6)\cdot MeCN$, **5**·MeCN

Zn(1) ··· Zn(2)	3.038(1)	Zn(2)–O(1)	2.055(3)
Zn(1)–O(1)	2.074(3)	Zn(2)–O(2)	2.079(3)
Zn(1)–O(2)	2.036(3)	Zn(2)–O(4)	2.007(3)
Zn(1)–O(3)	2.011(3)	Zn(2)–N(3)	2.039(4)
Zn(1)–N(1)	2.030(4)	Zn(2)–N(4)	2.054(4)
Zn(1)–N(2)	2.056(3)		
O(1)–Zn(1)–O(2)	76.61(11)	O(1)–Zn(2)–O(4)	97.98(12)
O(1)–Zn(1)–O(3)	94.99(12)	O(1)–Zn(2)–N(3)	88.10(13)
O(1)–Zn(1)–N(1)	87.60(13)	O(1)–Zn(2)–N(4)	146.39(13)
O(1)–Zn(1)–N(2)	160.02(13)	O(2)–Zn(2)–O(4)	94.37(12)
O(2)–Zn(1)–O(3)	100.36(12)	O(2)–Zn(2)–N(3)	156.48(13)
O(2)–Zn(1)–N(1)	146.81(14)	O(2)–Zn(2)–N(4)	88.03(13)
O(2)–Zn(1)–N(2)	89.35(13)	O(4)–Zn(2)–N(3)	105.12(14)
O(3)–Zn(1)–N(1)	110.07(13)	O(4)–Zn(2)–N(4)	112.81(13)
O(3)–Zn(1)–N(2)	101.55(13)	N(3)–Zn(2)–N(4)	96.19(14)
N(1)–Zn(1)–N(2)	97.06(14)	Zn(1)–O(1)–Zn(2)	94.73(11)
O(1)–Zn(2)–O(2)	76.08(11)	Zn(1)–O(2)–Zn(2)	95.14(12)

Template reaction of 2,6-diacetyl-4-methylphenol, $ZnCl_2$ and 1,2-diaminoethane afforded a yellow microcrystalline solid which readily precipitates from the reaction mixture. The IR spectrum of this compound shows a sharp, strong C=N stretching vibration at 1617 cm^{-1}, while elemental analytical data indicated a 1 : 1 : 1 ratio of Zn : L^4 : Cl. This product proved to be insoluble in a wide range of solvents. However, the same compound could be obtained when the template reaction is performed using $Zn(NO_3)_2\cdot 6H_2O$ or $Zn(OAc)_2\cdot 2H_2O$, followed by an anion metathesis using, for example, KCl. The metathesis procedure was found to be a more effective way to obtain a single crystal suitable for X-ray analysis or a pure bulk sample of the complex.

The molecular structure of $[Zn_2(L^4)Cl_2]$ **6** is shown in Fig. 6. with selected bond lengths and angles in Table 6. Each Zn^{II} centre is five coordinate and adopts a distorted square-pyramidal geometry with coordination to two imine N-donors [Zn(1)–N(1) and Zn(1)–N(2), 2.076(2), 2.062(2) Å], two bridging phenoxy O-donors [Zn(1)–O(1) and Zn(1)–O(1^i), 1.994(2), 2.072(2) Å, i = $-x+2$, $-y+1$, $-z$] and an axially ligated Cl^- ligand [Zn–Cl 2.2414(11) Å]. The symmetry equivalent Zn^{II} ions lie in opposite directions 0.788 Å out of the N_2O_2 least squares mean plane, with a Zn^{II}–Zn^{II} separation of 3.229(2) Å. As can be seen from these data, the coordination spheres of **1**

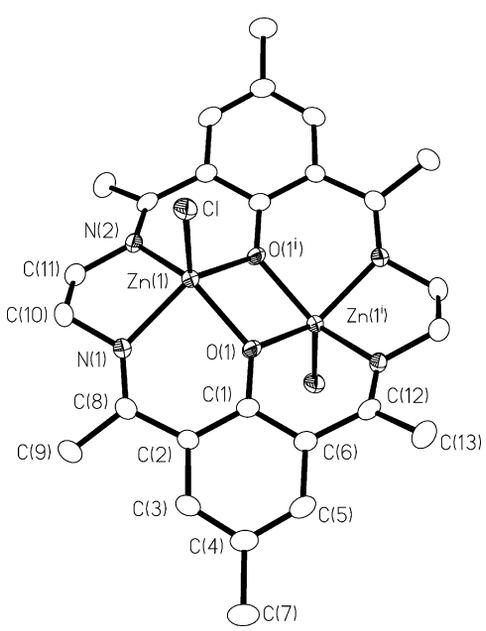

Fig. 6 An ORTEP view of **6** with 70% probability ellipsoids. Symmetry operation used to generate equivalent atoms: $2-x$, $1-y$, $-z$.

Table 6 Selected bond lengths [Å] and angles [°] for $[Zn_2(L^4)Cl_2]$, **6**

Zn–O(1)	1.994(2)	Zn–N(2)	2.062(2)
Zn–O(1^i)	2.072(2)	Zn–Cl	2.241(1)
Zn–N(1)	2.076(2)	Zn ··· Zn^i	3.229(2)
N(1)–Zn–N(2)	83.45(9)	N(2)–Zn–O(1^i)	82.30(8)
N(1)–Zn–Cl	112.30(7)	N(2)–Zn–Cl	105.54(7)
N(1)–Zn–O(1)	85.35(8)	O(1)–Zn–O(1^i)	74.86(9)
N(1)–Zn–O(1^i)	134.19(8)	O(1)–Zn–Cl	119.18(7)
N(2)–Zn–O(1)	134.84(8)	O(1^i)–Zn–Cl	113.44(6)

Symmetry code: i $-x+2$, $-y+1$, $-z$.

and **6** are closely related, and, as noted above, they are very similar to the previously reported 1,2-cyclohexanediamine bridged macrocyclic complex.[9] This suggests that the N_2O_2 compartments of the C_2-bridged macrocyclic ligands are too small to accommodate the Zn^{II} centres as in all these compounds the metal ion is *ca*. 0.78 Å out of the N_2O_2 plane.

Conclusions

We have shown that the reaction of simple diamines with 2,6-diformyl-4-methylphenol in the presence of $Zn(OAc)_2$ leads to the synthesis of a series of complexes of stoichiometry $Zn_2(L)(OAc)_2$. Mass spectral and NMR data are very similar for **1**, **2** and **3** indicating the production of the [2 + 2] cyclisation ligands in all three cases. IR spectral evidence suggested differences between the bonding modes of the acetates in the C_2- and C_3-linked complexes compared to the C_4-bridged complex. This was confirmed by single crystal X-ray structure determinations. Increasing the size of the cavity and the flexibility of the ligand by using a longer diamine therefore affords a significantly different product. In complex **3** the macrocyclic ligand adopts a very twisted conformation which allows one of the acetate moieties to bridge the two Zn^{II} ions.

We have also confirmed that the product of the reaction of $Zn(OAc)_2\cdot 2H_2O$ with pre-formed ligands differs from those of one-pot template reactions of $Zn(OAc)_2\cdot 2H_2O$ with the component aldehyde and amine. Thus, the template reaction of $Zn(OAc)_2\cdot 2H_2O$ with 2,6-diacetyl-4-methylphenol and 1,2-diaminoethane gives the complex of the formula $[Zn_2(L^4)(OAc)_2]$[15] whereas the reaction of $Zn(OAc)_2\cdot 2H_2O$ with $[H_4L^4](PF_6)_2$ gives the mononuclear complex $[Zn(H_2L^4)(MeCN)](PF_6)_2$. The template reaction of $Zn(OAc)_2\cdot 2H_2O$ with 2,6-diformyl-4-methylphenol and 1,3-diaminopropane gives $[Zn_2(L^2)(OAc)_2]$ whereas reaction of $Zn(OAc)_2\cdot 2H_2O$ with $[H_4L^2](PF_6)_2$ gives $[Zn_2(L^2)(OAc)](PF_6)$. We believe this to be due to either the synthesis of the kinetic reaction product under the conditions employed or to preferential packing effects gained from the spherical PF_6^- counter-anion.

Current work seeks to develop further routes to these pre-formed ligand and complexes as metal cation extractants.[13]

Experimental

General

All materials were reagent grade and were used as received. 2,6-Diformyl-4-methylphenol was prepared by a modified route from that reported originally by Ullmann and Brittner[16] and then modified by Gagné *et. al.*[17] 2,6-Diacetyl-4-methylphenol was prepared by a modified literature method.[18] Elemental analyses (C, H and N) were carried out using the University of Nottingham Microanalytical Service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1600 Fourier-transform infrared spectrophotometer. NMR spectra were recorded using a Bruker DPX300 spectrometer. Positive-ion FAB mass spectra were recorded on a Kratos MS 50TC spectrometer with 3-nitrophenol or glycerol as the matrix solvent.

Synthesis of ligands

$[H_4L^4](PF_6)_2$. To a solution of 2,6-diacetyl-4-methylphenol (2.08 mmol) in MeOH (45 cm^3) was added 1,2-diaminoethane (2.84 mmol) followed by HBr (0.30 cm^3, 48% solution). The solution was heated to reflux for 3.5 h. The yellow solution was then filtered hot before immediate addition of NH_4PF_6 (2.52 mmol). The yellow solid that precipitated was collected by filtration, washed with diethyl ether and dried under suction; yield 61%. Found: C, 42.87; H, 4.42; N, 7.65; $C_{26}H_{34}N_4F_{12}O_2P_2$ requires C, 43.09; H, 4.70; N, 7.73%. IR (KBr disc): 3422w, 2925w, 2867w, 2689w, 1627s, 1542s, 1444m, 1417m, 1378s, 1269s, 1167w, 1089w, 992m, 832s, 650w, 559s, 477m, 418w cm^{-1}. NMR spectra (CD_3CN): δ_H 16.49 (br s, 4H, NH), 8.03 (s, 4H, Ar-H), 4.20 (s, 8H, CH_2), 2.69 (s, 12H, CH_3), 2.36 (s, 6H, CH_3); δ_C 180.03 (CH=N), 174.36 (Ar-C), 140.65 (Ar-C), 123.82 (Ar-C), 117.61 (Ar-C), 44.84 (NCH_2), 19.31 (Ar–CH_3) and 15.37 (CH_3C=N). FAB MS (3-NOBA): *m/z* 433, $[C_{26}H_{33}N_4O_2]^+$, 579, $[C_{26}H_{34}N_4O_2](PF_6)^+$

$[H_4L^2](PF_6)_2$. $[H_4L^2](PF_6)_2$ was prepared by an analogous route to $[H_4L^4](PF_6)_2$ except that the product was recrystallised from MeCN and diethyl ether. Yield 66%. Found: C, 39.5; H, 4.41; N,8.83. $C_{24}H_{30}N_4O_2P_2F_{12}.CH_3NO_2$ requires: C, 39.6; H,4.39; N,9.25%. IR (KBr disc): 3674w, 3588w, 2959m, 2878w, 1670s, 1651s, 1534s, 1460m, 1421w, 1399w, 1367m, 1346m, 1286w, 1248s, 1120m, 1076w, 1027m, 1005m, 911w, 832s, 740w, 676w, 615w, 557s, 471w and 416w cm^{-1}. NMR spectra (CD_3CN): δ_H 13.50 (br s, 4H, NH), 8.30 (4H, br s, C(N)H), 7.30 (4H, s, Ar-H), 4.04 (8H, br m, CH_2), 2.32 (4H, m, CH_2) and 2.01 (6H, s, CH_3); δ_C 177.13 (CH=N), 167.8 (Ar-C), 146.00 (Ar-C), 123.73 (Ar-C), 116.75 (Ar-C), 51.89 (NCH_2), 26.93 ($CH_2CH_2CH_2$) and 18.53 (Ar–CH_3). FAB (3-NOBA): *m/z* 405, $[C_{24}H_{29}N_4O_2]^+$, 551, $[C_{24}H_{30}N_4O_2](PF_6)^+$.

Synthesis of Zn^{II} complexes

$[Zn_2(L^1)(OAc)_2]$ 1, $[Zn_2(L^2)(OAc)_2]$ 2 and $[Zn_2(L^3)(OAc)(\mu\text{-}OAc)]$ 3. To a solution of 2,6-diformyl-4-methylphenol (1 mmol) in MeOH (10 cm^3) was added $Zn(OAc)_2{\cdot}2H_2O$ (1 mmol) in $CHCl_3$ (15 cm^3) at 0 °C. A bright yellow solution was formed. The diamine (1 mmol) was dissolved in $CHCl_3$ (10 cm^3) and was added dropwise with stirring. The solution was then heated to reflux for 6 h. After filtration to remove any insoluble impurities, the filtrate was evaporated to dryness by rotary evaporation to leave a yellow residue. This solid was dissolved in $CHCl_3$ and filtered. Addition of Et_2O to the solution caused precipitation of a solid. This solid was filtered off, washed with diethyl ether and dried under suction. Crystals of **1**·2$CHCl_3$ suitable for X-ray diffraction studies were grown by allowing a $CHCl_3$ solution of **1** evaporate slowly for 5 days. Crystals of **2**·2$CHCl_3$ and **3**·$CHCl_3$ suitable for X-ray diffraction studies were obtained by diethyl ether diffusion into chloroform solution over 12 h.

1. Yield 28%. IR (KBr disc): 3423br, 2911w, 1637s, 1542s, 1443m, 1391m, 1330m, 1232w, 1174w, 1090w, 1033m, 996w, 926w, 926w, 886w, 838w, 799w, 778w, 759w, 677w, 618w, 578w, 560w, 533w and 489w cm^{-1}. NMR spectra ($CDCl_3$): δ_H (300 MHz) 8.45 (s, 4H, HC=N), 7.25 (s, 4H, Ar-H), 4.06 (br t, 8H, CH_2), 2.26 (s, 6H, PhCH_3) and 1.80 (s, 6H, CH_3); δ_C 178.8 (CH_3CO_2), 166.0 (CH=N), 165.0 (Ar-C), 138.3 (Ar-C), 124.6 (Ar-C), 122.9 (Ar-C), 54.1 (NCH_2), 22.2 (CH_3) and 19.9 (CH_3). FAB MS (3-NOBA) *m/z* 563, $[Zn_2C_{24}H_{25}N_4O_2]^+$, 505, $[Zn_2C_{22}H_{22}N_4O_2]^+$.

2. Yield 66%. Found: C, 51.33; H, 5.04; N, 8.61. $C_{28}H_{32}N_4O_6Zn_2$ requires C, 51.62; H, 4.96; N, 8.60%. IR (KBr disc) 3380br, 2925m, 2858w, 1638s, 1609s, 1559s, 1438s, 1411s, 1332s, 1280m, 1238m, 1195m, 1126m, 1084m, 1043w, 1001w, 932w, 876w, 812m, 775w, 666w, 617w, 589w, 529w, 508w, 485w and 413w cm^{-1}. NMR spectra (CD_3OD): δ_H 8.41 (s, 4H, HC=N), 7.42 (s, 4H, Ar-H), 4.06 (br t, 8H, CH_2), 2.33 (s, 6H, CH_3), 2.05 (br m, 8H, CH_2) and 1.86 (s, 6H, CH_3); δ_C 178.79 (CH_3CO_2), 170.32 (CH=N), 165.63 (Ar-C), 141.99 (Ar-C), 125.39 (Ar-C), 121.01 (Ar-C), 63.01 (CH_2), 29.45 (CH_2), 22.54 (CH_3) and 18.35 (CH_3). FAB MS NOBA): *m/z* 591, $[Zn_2C_{26}H_{29}N_4O_2]^+$, 531, $[Zn_2C_{24}H_{26}N_4O_2]^+$.

3. Yield 90%. IR (KBr disc) 3425br, 2927br, 1633s, 1603m, 1553m, 1449m, 1408m, 1337m, 1221w, 1111w, 1056w, 1018m, 917w, 815w, 768w, 757w, 670w, 619w, 563w, 522w, 492w, 445w cm^{-1}. NMR spectra (CD_3OD): δ_H 8.52 (s, 4H, HC=N), 7.44 (s, 4H, aromatic H), 3.84 (br s, 8H $CH_2CH_2CH_2CH_2$), 2.34 (s, 6H, CH_3), 2.05 (br s, 4H, $CH_2CH_2CH_2CH_2$), 1.92 (s, 6H, CH_3); δ_C 176.97 (CH_3CO_2), 170.09 (CH=N), 165.93 (Ar-C), 141.14 (Ar-C), 124.60 (Ar-C), 121.33 (Ar-C), 59.65 (CH_2), 27.54 (CH_2), 23.09 (CH_3) and 19.89 (CH_3). FAB MS (glycerol–MeOH–H_2O): *m/z* 619, $[Zn_2C_{28}H_{33}N_4O_2]^+$, 561, $[Zn_2C_{26}H_{30}N_4O_2]^+$.

$[Zn(H_2L^4)(MeCN)](PF_6)_2$ 4. To a solution of $[H_4L^4](PF_6)_2$ (0.30 mmol) in MeCN (20 cm^3) was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.65 mmol) in MeOH (14 cm^3). The solution was heated to reflux for 10 min after which a small amount of yellow solid had precipitated. This solid was removed by filtration and the filtrate concentrated by rotary evaporation. The addition of diethyl ether caused a yellow emulsion to form, from which a finely powdered yellow solid precipitated on cooling at 253 K for 30 min; yield 91%. The product was recrystallised form MeCN–diethyl ether. The crystallographic sample was obtained by diethyl ether diffusion into a acetonitrile solution of the complex at room temperature. Found: C, 40.31; H,4.21; N, 8.19. $C_{28}H_{35}N_5O_2P_2F_{12}Zn$ requires C, 40.56, H, 4.23; N, 8.45%. IR (KBr disc) 3567w, 2931w, 1624 vs, 1559s, 1438m, 1399m, 1378m, 1356m, 1272m, 1259m, 1208w 1167w, 1100w, 1081w, 996w, 844w, 800m, 740w, 683w, 617w, 558vs, 523w, 482w, 412w cm^{-1}. NMR spectra (CD_3CN): δ_H 2.32 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 2.75 (s, 6H, CH_3), 3.94 (s, 4H, CH_2), 4.21 (s, 4H, CH_2), 7.86 (d, 2H, Ar-H), 7.93 (d, 2H, Ar-H), 16.38 (br, 2H, NH). δ_C 15.72 (CH_3), 19.43 (CH_3), 19.69 (CH_3), 44.85 (CH_2), 49.65 (CH_2), 117.88 (Ar-C), 125.21 (Ar-C), 125.96 (Ar-C), 135.25 (Ar-C), 140.33 (Ar-C), 168.22 (Ar-C), 175.94, (CH=N), 180.37 (CH=N). FAB MS (3-NOBA) *m/z* 495, $[ZnC_{26}H_{30}N_4O_2]^+$, 433, $[C_{26}H_{33}N_4O_2]^+$.

$[Zn_2(L^2)(\mu\text{-}OAc)](PF_6)_2{\cdot}$MeCN, 5·MeCN. To a solution of $[H_4L^2](PF_6)_2$ (0.11 mmol) in MeCN (6 cm^3) was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.22 mmol) in MeOH (4 cm^3) to give a yellow solution. To this was added excess NaOAc (1.4 mmol). The solution was heated to reflux for 4 h and then allowed to cool to room temperature. The solvent was removed by rotary evaporation and the residue dissolved in MeCN and filtered. Slow evaporation of MeCN caused the precipitation of a yellow crystalline solid which collected by filtration and dried *in vacuo*; yield 66%. The crystallographic sample was obtained by diethyl ether diffusion into a acetonitrile solution of the complex at room temperature.

Found: C, 42.28; H, 3.91; N, 8.31. $C_{26}H_{32}N_5O_4F_6PZn_2$ requires: C, 42.35; H, 3.97; N, 7.60%. IR (KBr disc): 3648m, 3482m, 2936m, 2860w, 1637s, 1606m, 1573s, 1442s, 1415s, 1332m, 1281m, 1260w, 1239m, 1193w, 1124m, 1082m, 1044w, 999w, 931w, 840s, 773m, 740w, 669w, 618w, 589w, 558m, 527w and 508w cm^{-1}.

$[Zn_2(L^4)Cl_2]$, 6. To a solution of 2,6-diacetyl-4-methylphenol (0.192 g, 1 mmol) and 0.202 g (2 mmol) of triethylamine in MeOH (25 cm^3), 0.163 g (2 mmol) of $ZnCl_2$ dissolved in MeOH (5 cm^3) were added. The resulting yellow solution was stirred at for 15 min at 50 °C and then 0.06g (1 mmol) of 1,2-diaminoethane were added. After a few minutes a yellow precipitate appeared, the solution was held at reflux for 35 min, after which

Table 7 Crystallographic data summary

	1·2CHCl$_3$	**2**·2CHCl$_3$	**3**·CHCl$_3$	**4**	**5**·MeCN	**6**
Empirical formula	$C_{28}H_{30}Cl_6N_4O_6Zn_2$	$C_{30}H_{32}Cl_6N_4O_6Zn_2$	$C_{31}H_{37}Cl_3N_4O_6Zn_2$	$C_{28}H_{35}F_{12}N_5O_2P_2Zn$	$C_{28}H_{32}F_6N_5O_4PZn_2$	$C_{26}H_{30}Cl_2N_4O_2Zn_2$
M	862.00	888.04	798.74	828.92	778.30	632.18
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
a/Å	13.761(2)	7.416(2)	11.565(7)	15.34(2)	15.736(4)	7.352(4)
b/Å	11.358(2)	9.184(2)	12.732(3)	19.998(7)	12.177(5)	17.660(9)
c/Å	11.211(2)	14.217(3)	13.289(2)	21.537(12)	16.237(4)	9.967(5)
α/°	–	78.22(3)	112.75(3)	–	–	–
β/°	97.233(15)	85.11(4)	96.16(3)	–	98.85(2)	104.74(2)
γ/°	–	82.28(3)	108.63(3)	–	–	–
V/Å^3	1738.3(5)	937.6(4)	1649.2(11)	6607(10)	3074.2(17)	1251.5(11)
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pbca$	$P2_1/n$	$P2_1/c$
Z	2	1	2	8	4	2
μ/mm^{-1}	1.887	1.752	1.747	0.945	1.693	2.163
Independent reflections	3067	3296	4650	5804	5411	1631
Reflections with $I > 2\sigma(I)$	2736	2961	3524	4633	4401	1480
Final R_1 [$F > 4\sigma(F)$], wR_2 [all F^2]	0.0425, 0.111	0.0398, 0.104	0.0650, 0.187	0.0709, 0.177	0.0464, 0.101	0.0216, 0.0563

Details in common: T = 150 K; refinement based on F^2.

time the product was filtered off and washed with $CHCl_3$, MeOH and diethyl ether, and dried *in vacuo* yielding 0.270 g of a yellow powder, 87% yield. Found: C, 49.17, H, 4.74, N, 8.84. $C_{26}H_{30}Cl_2N_4O_2Zn_2$ requires C, 49.39, H, 4.78; N, 8.86%. IR (KBr disc): 2956w, 1617s, 1597s, 1536s, 1421s, 1417s, 1360m, 1349m, 1330m, 1298m, 1286m, 1179s, 1609m, 878m, 819m, 794w, 781w, 623w, 519m, 488m. The crystallographic sample was obtained as a by-product in the attempted synthesis of a ruthenium macrocycle and was originally refined as being $[Ru_2(L^4)Cl_2]$.[12] Further analysis confirmed this original assignment of the metal ion to be in error. Crystals of the same quality can be obtained on standing *via* anion metathesis of a solution of $[Zn_2(L^4)(OAc)_2]$ (prepared as for **6** but using $Zn(OAc)_2{\cdot}2H_2O$), by addition of saturated KCl in MeOH.

Crystallography

Crystal data and summaries of the crystallographic analyses for all the complexes are given in Table 7. Diffraction data were collected on a Stoë Stadi-4 diffractometer equipped with an Oxford Cryosystems open-flow cryostat[19] using ω–θ scans and graphite monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarisation effects. The structures were fully solved by direct methods using SHELXS 97[20] and full-matrix least squares refinement undertaken using SHELXL 97.[21] The hydrogen atoms were included at idealised positions and allowed to ride on their parent atoms with the exception of the methyl H atoms which were located from circular difference Fourier synthesis and thereafter refined as part of rigid CH_3 groups. In general all non-hydrogen atoms were refined anisotropically. Molecular structures were generated using ORTEP.[22]

During the early stages of the refinement of **4** it was found that the Zn^{II} ion was disordered between two cavities of the macrocycle. At convergence the site occupancy was found to be 0.899(2) for Zn(1) and 0.101(2) for Zn(2). In addition, some disorder of the PF_6^- anions was observed. Static disorder models were investigated but were found unsuitable. The geometric and displacement parameters of both PF_6^- anions were subject to reasonable restraints. H1N3 and H1N4 were observed in difference maps and refined with restraints. During refinement of **5**·MeCN it was found that the PF_6^- anion was disordered and this was modelled by resolving each of the 'equatorial' fluorines (F2–F4, F2′–F4′) into two orientations and refining their occupancies. The geometry of the disordered anion was subject to reasonable restraints.

CCDC reference numbers 197068–197072 and 199496.

See http://www.rsc.org/suppdata/dt/b2/b210936k/ for crystallographic data in CIF or other electronic format.

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References

1 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.

2 For examples see: B. F. Hoskins, R. Robson and G. A. Williams, *Inorg. Chim. Acta*, 1976, **16**, 121; C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagné and D. H. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229; R. Das, K. K. Nanda, I. Paul, S. Baitalik and K. Nag, *Polyhedron*, 1994, **13**, 2639; B. F. Hoskins and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2593; S. K. Mandal, L. K. Thompson, M. J. Newlands and E. J. Gabe, *Inorg. Chem.*, 1989, **28**, 3707; L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson and M. K. Park, *Inorg. Chem.*, 1996, **35**, 3117; S. K. Mandal, L. K. Thompson, M. J. Newlands, E. J. Gabe and K. Nag, *Inorg. Chem.*, 1990, **29**, 1324; H. Furutachi and H. Okawa, *Inorg. Chem.*, 1997, **36**, 3911; J. Nisho, H. Okawa, S-I. Ohtsuka and M. Tomono, *Inorg. Chim. Acta*, 1994, **218**, 27; V. McKee and S. S. Tandon, *Inorg. Chem.*, 1989, **28**, 2902; R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; S-I. Ohtsuka, M. Kodera, K-I. Motoda, M. Ohba and H. Okawa, *J. Chem. Soc., Dalton. Trans.*, 1995, 2599; H. Okawa, M. Tadokoro, Y. Aratake, M. Ohba, K. Shindo, M. Mitsumi, M. Kiokawa, M. Tomono and D. E. Fenton, *J. Chem. Soc., Dalton. Trans.*, 1993, 253; H. Okawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida and D. E. Fenton, *Inorg. Chem.*, 1993, **32**, 2949; H. Wada, T. Aono, K-I. Motoda, M. Ohba, N. Matsumoto and H. Okawa, *Inorg. Chim. Acta.*, 1996, **246**, 13; H. Wada, K-I. Motoda, M. Ohba, H. Sakiyama, N. Matsumoto and H. Okawa, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1105.

3 A. J. Atkins, A. J. Blake and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1993, 1662; N. D. J. Branscombe, A. J. Blake, A. Marin-Becerra, W-S. Li, S. Parsons, L. Ruiz-Ramirez and M. Schröder, *Chem. Commun.*, 1996, 2573; S. Brooker and P. D. Croucher, *J. Chem. Soc., Chem. Commun.*, 1995, 2075; S. Brooker, P. D. Croucher and F. M. Roxburgh, *J. Chem. Soc., Dalton. Trans.*, 1996, 3031; S. Brooker and P. D. Croucher, *Chem. Commun.*, 1997, 459.

4 H. Okawa and H. Sakiyama, *Pure Appl. Chem.*, 1995, **67**, 2273; H. Wada, K. Motoda, M. Ohba, H. Sakiyama, N. Matsumoto and H. Okawa, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1105; T. Aono, H. Wada, M. Yonemura, M. Ohba, H. Okawa and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1997, 1527.

5 E. Hough, L. K. Hanson, B. Birknes, K. Jynge, S. Hanson, A. Hardvik, C. Little, E. Dodson and Z. Derewenda, *Nature*, 1989, **338**, 357; S. K. Burley, P. R. David, A. Taylor and W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA*, 1990, **87**, 6879; *Bioinorganic Chemistry*,

University Science Books, ed. I. Bertini, H. B. Gray and S. J. Lippard, 1994, p. 37.
6 H. Adams, N. A. Bailey, P. Bertrand, C. O. Rodriguez de Barbarin, D. E. Fenton and Shaohua Gou, *J. Chem. Soc., Dalton Trans.*, 1995, 275.
7 W. Huang, S. Gou, D. Hu, Y. Xu, S. Chantrapromma and Q. Meng, *J. Mol. Struc.*, 2001, **561**, 121.
8 W. Huang, S. Gou, D. Hu, S. Chantrapromma, Hoong-Kun Fun and Q. Meng, *Inorg. Chem.*, 2001, **40**, 1712; W. Huang, S. Gou, D. Hu, S. Chantrapromma, Hoong-Kun Fun and Q. Meng, *Inorg. Chem.*, 2002, **41**, 864.
9 S. R. Korupoju, N. Mangayarkarasi, S. Ameerunisha, E. J. Valente and P. S. Zacharias, *J. Chem. Soc., Dalton Trans.*, 2000, 2845.
10 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 3603.
11 E. Asato, H. Furutachi, T. Kawahashi and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1995, 3897.
12 A. J. Atkins, A. J. Blake and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1993, 353; A. J. Atkins, D. Black, A. J. Blake, A. Marin-Becerra, S. Parsons, L. Ruiz-Ramirez and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1996, 457.
13 D. Black, A. J. Blake, R. L. Finn, L. F. Lindoy, A. Nezhadali, G. Rougnaghi, P. A. Tasker and M. Schröder, *Chem. Commun.*, 2002, 340.
14 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 3rd edn., 1978, p. 232.
15 N. A. Bailey, D. E. Fenton, P. B. Roberts and A. M. Walford, *J. Chem. Soc., Dalton Trans.*, 1987, 1865.
16 F. Ullmann and K. Brittner, *Chem. Ber.*, 1909, **42**, 2539.
17 R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073.
18 S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429.
19 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
20 G. M. Sheldrick, SHELXS 97, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
21 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.
22 C. K. Johnson, ORTEP-II: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.