Synthesis, Structure and Hydrolytic Properties of a Family of New Zn Complexes Containing Hexaazamacrocyclic Ligands

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The synthesis, structure and spectroscopic properties of a family of Zn complexes containing a dinucleating hexaazamacrocyclic ligand (L) and anionic ligands (X) of general formula $[Zn_2(X)_{4-n}(L)]^{n+}$ (**1**–**8**; L = H2p, H3p, Me2p, Me2m, Me3p, Me3m; X = Cl, n = 0; X = NO_3, n = 2) have been investigated. The solid-state structural characterisation has been performed by means of X-ray diffraction analysis for complexes **3**, **5**, **7·1/3CH$_2$Cl$_2$** and **8**. The Zn complexes **5**, **7·1/3CH$_2$Cl$_2$** and **8** containing chloride ligands present a distorted N_2Cl_2 tetrahedral coordination with two non-coordinated N atoms of the macrocyclic ligand. On the other hand, complex **3**, which contains nitrate ligands, displays an N_3O_2 pentacoordination with all the N atoms of the macrocyclic ligand bonded to the metal centres. The different factors governing the relative Zn–Zn disposition are discussed. NMR spectroscopy in solution reveals the presence of fluxional behaviour and a completely different structural arrangement than in the solid state. In particular, evidence for the formation and breaking of Zn–N bonds involving all the macrocyclic ligand aminic N atoms is obtained for the chloride complexes **2** and **4**–**8**. Finally, complexes **1**, **3**, **5** and **7** hydrolyse *p*-nitrophenyl acetate (NA) with second-order rate constants ranging from 0.045 to 0.193 $M^{-1}s^{-1}$, thus manifesting the influence of the ligands over the hydrolytic activity.

Introduction

Macrocyclic polyamines are well-known to participate in molecular recognition phenomena with different kinds of substrates, such as organic and inorganic cations, anions and neutral molecules.[1] Such interactions have attracted interest from environmental, catalytic and health-related domains.[2] Macrocyclic molecules containing two polyamine units linked by a spacer are also capable of ligating two metal atoms in close proximity. In some cases this leads to interactions between the two metallic centres that results in interesting magnetic,[3] electronic[4,5] and/or catalytic properties.[6–8] The ability of macrocyclic ligands to preorganise two metal centres at a particular distance has also been used in the design of Zn complexes that efficiently catalyse the hydrolysis of phosphate and carboxy esters[9–11] thus mimicking the activity of zinc enzymes that mediate hydrolytic reactions.[12–16] However, exhaustive characterisation of Zn complexes with macrocyclic polyamines is scarce. In this work we have synthesised and characterised a series of Zn complexes with hexaazamacrocyclic ligands where the metal coordination and the metal-metal relative disposition are modulated by the characteristics of the macrocyclic ligand. We have also studied the ability of these complexes to perform the hydrolysis of *p*-nitrophenyl acetate (NA). Our results demonstrate that small changes in the macrocyclic backbone lead to important changes in the Zn−Zn distance and in the hydrolytic ability manifested by the complexes.

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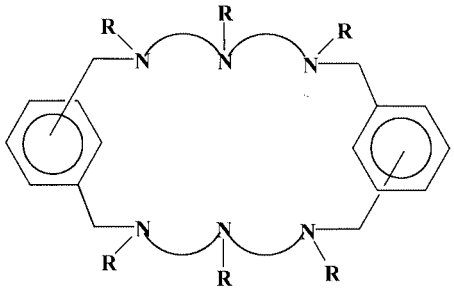
Results and Discussion

Synthesis and Solid-State Structure

The six macrocyclic ligands used in this work are shown in Scheme 1 and were prepared according to literature procedures.[17–20] This family of ligands comprises secondary amines and their hexamethylated analogues and is



		= $(CH_2)_n$	
		$n = 2$	$n = 3$
R = H	*p*	**H2p**	**H3p**
R = Me	*p*	**Me2p**	**Me3p**
	m	**Me2m**	**Me3m**

Scheme 1. Macrocyclic ligands used in this work

characterised by the number of methylenic units linking the amines, which can be two or three, and by the aromatic substitution that takes place in the *meta* or *para* positions.

Reaction of those ligands at room temperature with two times the stoichiometric amount of the appropriate Zn^{II} salt in methanol affords the corresponding dinuclear Zn^{II} complexes **1**−**8** as white microcrystalline solids in modest to good yields (ranging from 34 to 77%), as shown in Equation (1) for the particular case of **5**.

$$\text{Me2p} + 2\ ZnCl_2 \xrightarrow{\text{MeOH}} [Zn_2Cl_4(\text{Me2p})] \quad (1)$$

The crystal structures of $[Zn_2(NO_3)_2(H3p)](NO_3)_2$ (**3**), $[Zn_2Cl_4(Me2p)]$ (**5**), $[Zn_2Cl_4(Me3p)]\cdot 1/3CH_2Cl_2$ (**7·1/3CH$_2$Cl$_2$**) and $[Zn_2Cl_4(Me3m)]$ (**8**) have been determined by means of single-crystal X-ray diffraction analysis. Table 1 contains their crystallographic data whereas Table 2 contains their selected bond lengths and angles. Figure 1 shows the ORTEP diagrams obtained for the cationic molecular structure of complex **3** (top left) and the neutral molecular structures of complexes **5** (top right), **7** (bottom left) and **8** (bottom right), together with the atom labelling system used.

The cationic part of **3** consists of the macrocyclic ligand, which binds to two zinc atoms, and an NO_3^- anion bonded to each metal adopting an (η^2-*O*,*O*-NO_3) chelating mode (Δr_{Zn-O} = 0.075 Å). The whole molecule has an inversion centre that relates the metal atoms and half of the macrocyclic ligand with the other half. The Zn metal centres are five-coordinate, binding to three N atoms from the macrocyclic ligand and two oxygens from the nitrate ligand. The Zn−N distances range from 1.992(6) to 2.054(7) Å and the two Zn−O bonds are significantly different [Zn−O1: 2.206(8) Å; Zn−O2: 2.281(9) Å], although all of them compare well with the observed values of complexes containing an N_3ZnO_2NO coordination environment.[21] The N−Zn−N bond angles range from 92.5(3)° to 128.1(3)° whereas the N−Zn−O angles range from 89.3(3)° to 141.0(3)°, reflecting the distortions imposed by the rigidity of the macrocyclic ligand and the asymmetry of the coordinated nitrate anion.

Table 1. Crystallographic data of **3**, **5**, **7** and **8**

Complex	**3**	**5**	**7·1/3CH$_2$Cl$_2$**	**8**
Empirical formula	$C_{28}H_{46}N_{10}O_{12}Zn_2$	$C_{30}H_{52}Cl_4N_6Zn_2$	$C_{34.33}H_{58.67}Cl_{4.67}N_6Zn_2$	$C_{34}H_{60}Cl_4N_6OZn_2$
Mol. mass (g/mol)	845.49	769.42	851.71	825.42
Crystal system	orthorhombic	monoclinic	hexagonal	monoclinic
Space group	Pbca	$P2_1/n$	$R\bar{3}$	$P2_1/c$
Crystal size (mm^3)	0.09 × 0.2 × 0.4	0.05 × 0.3 × 0.4	0.2 × 0.2 × 0.1	0.15 × 0.3 × 0.45
a (Å)	14.1458(12)	10.9716(7)	22.9991(14)	10.7508(9)
b (Å)	15.3309(13)	8.0318(5)	22.9991(14)	12.2409(8)
c (Å)	16.2605(14)	20.9911(13)	21.7424(15)	14.8889(13)
β (deg)	90	101.144(8)	120	95.772(10)
Volume (Å^3)	3526.4(5)	1814.9(2)	9960.0(11)	1949.4(3)
Z	4	2	9	2
Temperature (K)	296(2)	223(2)	223(2)	293(2)
λ(Mo-K_α) (Å)	0.71073	0.71073	0.71073	0.71073
$\rho_{calcd.}$ (g/cm^3)	1.593	1.408	1.278	1.406
μ (mm^{-1})	1.436	1.570	1.395	1.537
Meas. reflns.	17342	13530	23527	15306
Unique reflns.	3109	3513	4297	3579
Observed reflns. [$I > 2\sigma(I)$]	1713	2403	1823	1990
Parameters	216	194	211	211
$R1$ [$I > 2\sigma(I)$][a]	0.076	0.0298	0.0402	0.0332
$wR2$ (all data)[b]	0.24	0.0681	0.0949	0.0699

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)\}^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (°) for **3**, **5**, **7** and **8**

	3	**5**	**7**·1/3CH_2Cl_2	**8**
Zn(1)−N(1)	2.042(6)	2.100(2)	2.088(4)	2.088(3)
Zn(1)−N(2)	2.054(7)	2.1194(19)	2.077(3)	2.108(2)
Zn(1)−N(3)	1.992(6)			
Zn(1)−Cl(1)		2.2153(7)	2.2395(15)	2.2103(9)
Zn(1)−Cl(2)		2.2092(7)	2.1888(14)	2.2266(9)
Zn(1)−O1	2.206(8)			
Zn(1)−O2	2.281(9)			
Zn(1)−Zn(1′)	8.73	12.395	10.744	6.743
N(1)−Zn(1)−N(2)	92.5(3)	87.38(7)	100.72(14)	100.95(10)
N(1)−Zn(1)−N(3)	128.1(3)			
N(2)−Zn(1)−N(3)	98.4(3)			
Cl(2)−Zn(1)−Cl(1)		121.19(3)	115.14(6)	119.12(4)
N(1)−Zn(1)−Cl(2)		112.49(6)	121.37(12)	105.49(7)
N(2)−Zn(1)−Cl(2)		111.02(6)	107.90(11)	108.70(7)
N(1)−Zn(1)−Cl(1)		108.58(6)	104.74(11)	113.59(7)
N(2)−Zn(1)−Cl(1)		111.08(5)	104.97(11)	107.42(7)
N(1)−Zn(1)−O(1)	94.9(3)			
N(1)−Zn(1)−O(2)	125.2(3)			
N(2)−Zn(1)−O(1)	141.0(3)			
N(2)−Zn(1)−O(2)	89.7(3)			
N(3)−Zn(1)−O(1)	106.6(3)			
N(3)−Zn(1)−O(2)	105.6(3)			
O(1)−Zn(1)−O(2)	55.3(3)			

Upon coordination, the macrocyclic ligand generates four six-membered rings containing the Zn metal, which, in all cases, adopt a chair conformation. The aromatic rings are oriented in a parallel manner and the coordinated nitrates are disposed in an *anti* configuration, as expected from a steric viewpoint. Finally the Zn···Zn distance is 8.73 Å. The structure is completed by two non-coordinating nitrate anions which could only be refined isotropically. Two oxygen atoms of each nitrate are within H-bond range (2.95−3.1 Å) of the N atoms of the macrocyclic ligand, on the opposite side of the $N_3Zn(\eta^2$-*O*,*O*)NO_3 unit.

The molecular structures of **5**, **7** and **8** consist of a neutral Zn_2Cl_4L unit. The macrocyclic molecules are again centrosymmetric. In sharp contrast to the previous structure and related complexes described in the literature — $[Pd_2Cl_2(Me2p)](ClO_4)_2{\cdot}H_2O$,[22] $[Cu_2Cl_2(Me2p)](BPh_4)(ClO_4){\cdot}CH_3CN$,[23] $[Cu_2(Me2p)(CO)_2](ClO_4)_2{\cdot}2H_2O$ and $[Cu_2(Me2m)(t\text{BuNC})_2](CF_3SO_3)_2$ [24] — the Zn atoms adopt a distorted tetrahedral geometry coordinated to only four of the six available N atoms of the macrocyclic ligand; each Zn coordinates to two chlorine atoms and two adjacent N atoms of the macrocycle, leaving two benzylic amines of the macrocycle as non-coordinating. Binding of the metal ion to only two N atoms of the macrocycle in **5**, **7** and **8** probably reflects that formation of the second Zn−Cl bond, in combination with the release of the strain imposed by the macrocyclic ligand, can overcome the breakage of a rather weak $Zn-N_{tertiary}$ bond.[25]

The coordination of Zn1 to two adjacent macrocyclic N atoms results in a five- (**5**), or six-membered (**7** and **8**) chelate ring where the six-membered ring always adopts a chair conformation. The Zn bond lengths and angles are within the expected range for Zn polyaza complexes previously reported in the literature.[26] The number of atoms that form the chelate cycle dramatically affects the N1−Zn−N2 and Cl1−Zn−Cl2 angles. The six-membered chelate rings of **7** and **8** result in N1−Zn−N2 angles of 100.72(14)° and 100.95(10)°, slightly smaller than the corresponding Cl1−Zn−Cl2 angles [115.14(6)° and 119.12(4)°, respectively], whereas the more constrained five-membered ring formed in the ethylene-based macrocycle **5** forces a more acute N1−Zn−N2 angle [87.38(7)°], remarkably smaller than the corresponding Cl1−Zn−Cl2 angle [121.19(3)°]. These parameters indicate a significant distortion from a tetrahedral geometry in **5**, which is further evidenced by the dihedral angle of 80.80° formed between the planes described by N2−Zn1−Cl2 and N1−Zn1−Cl1. It is interesting to note here that in all the structures described in the present work the aromatic rings are disposed in a parallel manner. Finally, complex **7** cocrystallises with a third of a molecule of severely disordered CH_2Cl_2.

For dinuclear complexes containing hexaazamacrocyclic ligands, such as the ones described here, the "internal cavity" of the complex can be defined as the smallest macrocycle containing the two metals. For complexes with all N atoms coordinated to the metal centre, as in **3**, the cavity dimension, expressed in terms of the number of member units, is dependent on the aromatic substitution (the *para* case having an internal cavity with two more units than the *meta*) and independent of the number of methylenic units within the amines. On the other hand, with a partial coordination of the macrocyclic ligand, such as that obtained in complexes **5**, **7** and **8**, the internal cavity will now depend on both factors. Thus, complex **7**, containing the Me3p ligand, will have a larger internal cavity than **3**, its H3p analogue, due to the enlargement produced by the partial coor-

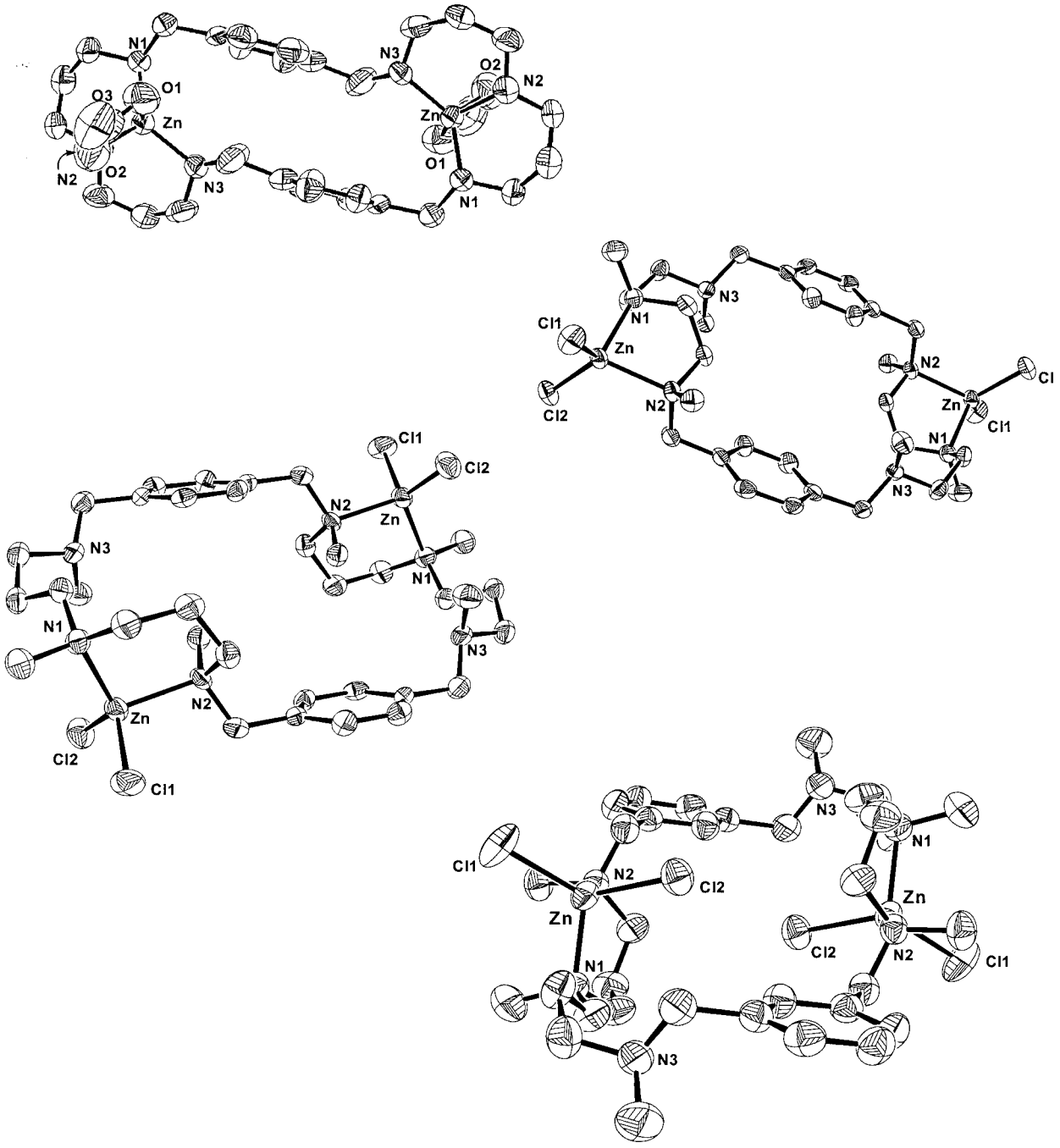


Figure 1. ORTEP diagram (50% probability) of the cationic part of complex **3** (top left), complex **5** (top right), complex **7** (bottom left) and **8** (bottom right)

dination of the former ligand. As a consequence the complex with the tertiary amine has a Zn···Zn distance larger than the corresponding secondary amine. Complex **5**, containing the Me2p ligand, has a smaller internal cavity than complex **7**, containing the analogous ligand but with propylene linkers instead of ethylene. In sharp contrast, **5** has a larger Zn···Zn distance than **7**, due to the relative disposition of the metal complexes produced by the methylene linkers. Finally, complex **8**, containing the Me3m ligand, which produces the largest internal cavity, presents the shortest Zn···Zn distance. This is due to the different arrangement that the *meta* aromatic substitution provokes with regard to the *para*, the former being more compact. As a consequence of this, in complex **8** (*meta* substitution) two of the Cl ligands bonded to the metal centres are directed towards the inside the cavity, whereas in complexes **5** and **7** (*para* substitution) all Cl ligands are clearly oriented outside the cavity and are pointing in opposite directions.

NMR Spectroscopy and Solution Structure

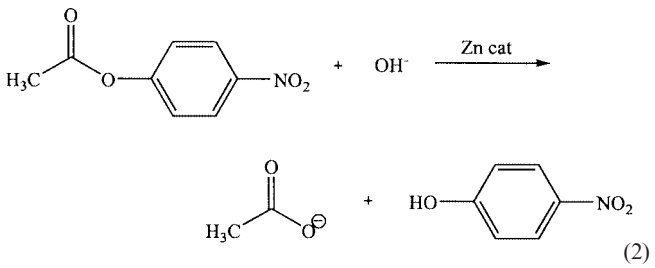
The ^1H and ^{13}C NMR spectra of complexes **1**−**7** at room temperature in different deuterated solvents are presented as Supporting Information and are assigned in the Exp. Sect. No NMR spectra could be obtained for complex **8** due to its low solubility.

In the spectra, the resonances are shifted downfield relative to the free ligand demonstrating that the metal ion remains bound to the macrocycle in solution. However, it is interesting to point out here that the fine structure of the spectra of these complexes is not well resolved either due to poor resolution of multiple superimposed signals or, more likely (vide infra), the presence of fluxional behaviour. The latter may be attributed to fast exchange between different conformers in solution, although these phenomena alone cannot explain the apparent simplicity of the spectra, which is not consistent with the more asymmetric structure of the complexes in the solid state, as determined by X-ray crystallography. If retained in solution, the structure determined in the solid state should give rise to two different signals (assuming fast aromatic ring rotation) for the aromatic protons in the complexes containing *para*-substituted macrocycles (**5** and **7**). In addition, the benzylic protons in **5**, **6** and **7** should also give rise to at least two different signals in a 1:1 ratio. However, the ^1H NMR spectra of **5** in CD_2Cl_2 (D_2O) and **7** in DMSO (D_2O) show only one broad singlet at δ = 7.39 (7.56) and 7.24 (7.47) ppm, respectively, indicating that all the aromatic protons are equivalent on the NMR timescale. The benzylic protons also appear as a broad singlet at δ = 3.78 (3.99) for **5**, 3.77 for **6** and 3.46 (3.91) ppm for **7**, which implies that the four benzylic groups are again equivalent. Thus, these symmetric spectra could either indicate the presence of a symmetric structure in solution, where the six N atoms participate in the simultaneous binding of the Zn atoms, or, alternatively, it may suggest the presence of two or more species in solution, such as the one determined by X-ray crystallography, undergoing fast inter-exchange. This process supposes rapid Zn−N bond formation and breaking involving all the amino nitrogen atoms of the ligand. This type of behaviour is not uncommon for d^{10} metal ions probably due to the lack of ligand field stabilisation.[27] Further support for the fluxional behaviour of the complexes is provided by variable temperature NMR spectroscopy of **5** in CD_2Cl_2 (Figure S10). The initially simple room temperature ^1H NMR spectra become complicated upon lowering the temperature. For example, the aromatic and benzylic protons, which appear as singlets at 295 K, convert into multiple poorly resolved signals. The higher complexity of the low temperature spectra is consistent with the freezing-out of the fluxional processes, although even at 160 K the signals do not became completely resolved, thus precluding a complete assignment of the spectra.

The spectra of **3** and **4**, which show two broad singlet signals, with a 5:3 integration ratio that are assigned to the benzylic protons, are also unusual. The data are consistent with at least two dramatically different isomeric forms of the complex. However, the singlet structure of the signals strongly suggests again the presence of fluxional behaviour and that each of the signals does not belong to a single species but to a number of inter-exchanging isomers. The solvent strongly influences the nature of the fluxional behaviour, as deduced from the sharpening of the resonances when using D_2O instead of CD_2Cl_2 or [D_6]DMSO. Even though the signals do not totally resolve, it is obvious that in aqueous solution the speed of the process is enhanced. Another interesting aspect of the chemistry of these complexes emerges when comparing the ^1H NMR spectra of complex **2** or **4** with **5** or **7**, respectively, in the same solvent — the comparison of the spectra of Zn complexes bearing secondary or tertiary amine macrocyclic ligands, showing a sharp narrowing for the latter. This observation favours the description of the fluxional behaviour as bond formation and breaking rather than a unique structure since it indicates that the breaking of the weaker $Zn-N_{tertiary}$ bonds[25] requires lower activation energies. Thus $Zn-N_{tertiary}$ bonds can form and break faster than the stronger $Zn-N_{secondary}$ analogues, finally resulting in the narrowing of the resonances.

Hydrolytic Activity

The Zn complexes containing *para*-substituted ligands (**1**, **3**, **5** and **7**) described in the present work were tested in the hydrolysis of 4-nitrophenyl acetate (NA) [Equation (2)]. The *meta* derivatives could not be used due to their low solubility in water. Figure 2A shows the linear dependency of the initial rate constant k_{in} (defined as v_{in}/[NA]) with regard to [$ZnCl_4$(Me2p)] (**5**) at different pH values ranging from 7.31 to 8.40; more-detailed kinetic data related to the hydrolysis of NA in the presence of different Zn complexes is included as Supporting Information in Table S1. As expected, the increase in pH results in a monotonical increase of k_{in}. This behaviour can be interpreted in terms of the generation of the nucleophilic LZn−OH species which has been shown to be the active species in previous works with related ligands.[11,28] This behaviour also rules out the possibility of the free metal ion being the active species since, as the pH is increased, its concentration strongly decreases. On the other hand blank experiments with only free ligand or free metal ion under similar conditions display a much smaller hydrolytic capacity. Furthermore, the free ligand is not observed in the NMR spectra of the complexes reported here. It is interesting to point out here that the rate constants observed for [$ZnCl_4$(Me3p)] (**7**) and for its nitrate analogue [$Zn(NO_3)_2$(Me3p)]$(NO_3)_2$ (data not shown) are



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virtually the same within experimental error. These results manifest the strong dependency of the rate constant with regard to the ligand system and, in contrast, the weak influence of the labile chloride and nitrate ligands.

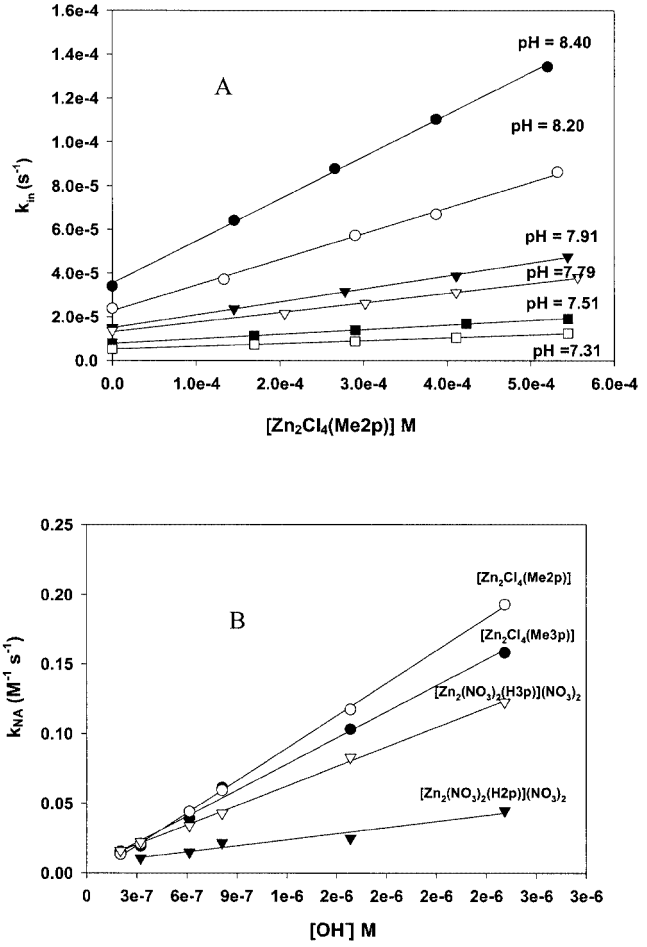

Figure 2. Kinetic data for the hydrolysis of 4-nitrophenyl acetate (NA) by the macrocyclic Zn complexes: A) initial rate constant k_{in} relative to [$ZnCl_4$(Me2p)] at different pH; B) second-order rate constants, k_{NA}, relative to [OH] for different macrocyclic Zn complexes

Unfortunately, in our case, at higher pH values the complexes start to precipitate out of the solution, preventing further kinetic analysis. A similar linear dependency is also found for complexes **1**, **3** and **7** and is presented as Supporting Information.

Second-order rate constants, k_{NA}, were obtained at a given pH from a plot of k_{in} vs. complex concentration. The linear dependency of this second-order rate constant against [OH] is shown in Figure 2B for the four *para* complexes. As can readily be seen, at a given pH complexes **5** (for instance at pH 8.4, k_{NA} = 0.193 $M^{-1}s^{-1}$) and **7** (0.158 $M^{-1}s^{-1}$), bearing tertiary amine ligands, give higher rate values than complexes **1** (0.045 $M^{-1}s^{-1}$) and **3** (0.123 $M^{-1}s^{-1}$) containing secondary amines. These values are about an order of magnitude lower than the best complexes reported in the literature for the same reaction under similar conditions,[28,29] although the low solubility of our complexes at pH's higher than 8.4 precludes a fair comparison.

Our results for the second-order rate constants are in agreement with tertiary amines generating more nucleophilic LZn−OH species than secondary amines due to the hydrophobicity of the former,[30] which precludes charge delocalisation among solvated species. When comparing complexes **5** and **7**, both with tertiary amines, at a given pH it is found that **5** has higher k_{NA} values than **7** even though the latter has four more methylenic groups. This is due to the fact that at the same pH the Me2p ligand generates a much higher concentration of LZn−OH species than Me3p, as has been previously shown in the literature for similar complexes.[31] Finally, for complexes bearing secondary amines the tendency is just the opposite than in the case of the tertiary amines just discussed. In particular, complex **1** presents significantly lower k_{NA} values than the rest of the studied complexes. At this moment it is not obvious to us why **1** has such a low hydrolytic activity, although, presumably, the structure of the ligand does not favour the interaction between the electrophile (Zn−OPO_2R) and nucleophile (Zn−OH) units.

Conclusion

A family of new dinuclear Zn complexes bearing hexaazamacrocyclic and chloride or nitrate ligands have been prepared and characterised from the corresponding metal salt and ligand as the starting materials. In the solid state, the metal coordination geometry as well as the ligand coordination mode are strongly dependent on the Zn starting material. Thus, $ZnCl_2$ generates a Cl_2N_2 tetrahedrally distorted environment for Zn with a coordination number (CN) of four whereas the $Zn(NO_3)_2$ salt generates an N_3O_2 environment with a CN of five. Furthermore the macrocyclic ligand in the former case coordinates through only four of the six possible N atoms, whereas in the latter case it coordinates through all its N atoms. These different coordination modes, together with the flexibility of the macrocyclic ligands, allows a certain control of the relative spatial Zn−Zn disposition.

NMR spectroscopy clearly indicates that the solution structure of these macrocyclic complexes is radically different from their structure in the solid state. In the case of the chloride complexes **2** and **4**−**8**, NMR spectroscopy reveals the presence of a fluxional behaviour that presumably involves exchange between conformational isomers and the formation and breaking of Zn−N bonds including all N atoms of the macrocyclic ligand.

Finally, complexes **1**, **3**, **5** and **7** have been shown to be capable of hydrolyzing *p*-nitrophenyl acetate (NA). Their different hydrolysis rates reveal how small variations in the ligand can significantly influence hydrolytic activity.

Experimental Section

Physical Methods: IR spectra were recorded on a Mattson-Galaxy Satellite FT-IR spectrophotometer as solid KBr pellets. Elemental

analyses were conducted on a Carlo−Erba Instrument, Mod. CHNS 1108. UV/Vis spectra were recorded on a Varian Cary-50 spectrophotometer, using quartz cuvettes. NMR spectra were recorded at 298 K on a Bruker DPX200 Model Avance (4.7 T) operating at 200 MHz for proton. Spectra were referenced to the residual protio solvent peaks or TMS (tetramethylsilane).

Electrospray ionisation mass spectra were acquired using a Navigator quadrupole instrument (MassLab Group, Finnigan, Manchester, UK) equipped with an Aqua system for atmospheric pressure chemical ionisation (APCI) and electrospray (ESI). The samples were introduced either with a liquid chromatographic pump (P2000, Thermo Separation Products) at a flow rate of 0.3 mL/min using different proportions of H_2O/methanol as the mobile phase, or by direct infusion by the Aqua system. Positive ion spectra were acquired in full scan 2−1600 *m*/*z* in continuum mode.

Materials and Synthesis: Solvents were purchased from SDS as synthesis grade. Acetonitrile was distilled from over P_2O_5 (Prolabo) and stored over molecular sieves. Diethyl ether and THF were distilled from over Na (Panreac) or benzophenone (Fluka), respectively, just previously to their use. CH_2Cl_2 was distilled from over CaH_2 (Aldrich) and stored over molecular sieves. Methanol was distilled from over Mg (Aldrich) and stored in the dark over molecular sieves. Acetone was dried over $CaCl_2$ (Panreac) and stored over molecular sieves.

The macrocyclic ligands 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]-triaconta-1(27),11(30),12,14(29),24(28),25-hexaene (**H2p**), 3,7,11,18,22,26-hexaazatricyclo[26.2.2.2^{13,16}]tetratriaconta-1(31),13(34),14,16(33),28(32),29-hexaene (**H3p**), 3,6,9,16,19,22-hexamethyl-3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]triaconta-1(27),11(30),12,14(29),24(28),25-hexaene (**Me2p**) 3,6,9,17,20,23-hexamethyl-3,6,9,17,20,23-hexaazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11,13,15(30),25,27-hexaene (**Me2m**), 3,7,11,18,22,26-hexamethyl-3,7,11,18,22,26-hexaazatricyclo[26.2.2.2^{13,16}]tetratriaconta-1(31),13(34),14,16(33),28(32),29-hexaene (**Me3p**) and 3,7,11,19,23,27-hexamethyl-3,7,11,19,23,27-hexaazatricyclo[27.3.1.1^{13,17}]tetratriaconta-1(33),13,15,17(34),29,31-hexaene (**Me3m**) were prepared according to the published procedures or slight modifications thereof.[17−20] (for structural drawing see Scheme 1).

[$Zn_2(NO_3)_2$(H2p)]$(NO_3)_2$·11/3H_2O (1·11/3H_2O): A methanol (3 mL) solution of $Zn(NO_3)_2$·6H_2O (179 mg, 0.60 mmol) was added dropwise to a vigorously stirred solution of H2p (123 mg, 0.30 mmol) in methanol (6 mL). A white precipitate rapidly appeared. The mixture was stirred for 30 min and then cooled down in an ice bath. The white solid that precipitated was then filtered, washed with methanol and dichloromethane and dried under vacuum. (168 mg, 0.21 mmol, 71%). FT-IR (KBr): ṽ, 3223, 2933, 2878 and 1383 cm^{-1}. $C_{24}H_{38}N_8O_6Zn_2$·11/3H_2O (855.5): calcd. C 33.70, H 5.34, N 16.37; found C 33.87, H 5.36, N 16.31. ^{1}H NMR (200 MHz, D_2O, 25 °C): δ = 2.50−3.20 (m, 16 H, NCH_2), 3.80−4.20 (m, 8 H, $ArCH_2$), 7.36 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, D_2O, 25 °C): δ = 45.9 (NCH_2), 52.0 ($ArCH_2$), 129.8 (arom. tert.), 136.6 (arom. quat.) ppm. MS: *m*/*z* = 727.56 [$Zn_2(NO_3)_2$(H2p)], 538.08 [$Zn(NO_3)$(H2p)].

[Zn_2Cl_4(H2p)]·4H_2O (2·4H_2O): A methanol (3 mL) solution of $ZnCl_2$ (28 mg, 0.20 mmol) was added dropwise to a vigorously stirred solution of H2p (41 mg, 0.10 mmol) in methanol (2.5 mL). A white precipitate rapidly appeared. The mixture was stirred for 30 min and then cooled down in an ice bath. The white solid that precipitated was then filtered, washed with methanol and dichloromethane and dried under vacuum. (25 mg, 0.04 mmol, 37%). $C_{24}H_{38}Cl_4N_6Zn_2$·4H_2O (755.3): calcd. C 38.17, H 6.14, N 11.13; found C 38.08, H 5.43, N 10.93. FT-IR (KBr): ṽ, 3217, 2930, 2874 and 1445 cm^{-1}. ^{1}H NMR (200 MHz, D_2O, 25 °C): δ = 2.50−3.20 (m, 16 H, NCH_2) 3.85 (m, 8 H, $ArCH_2$) 7.34 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, D_2O, 25 °C): δ = 47.8 (NCH_2), 55.3 ($ArCH_2$), 132.4 (arom. tert.), 139.3 (arom. quat.) ppm.

[$Zn_2(NO_3)_2$(H3p)]$(NO_3)_2$·4/3CH_3OH (3·4/3CH_3OH): A methanol (5 mL) solution of $Zn(NO_3)_2$·6H_2O (297 mg, 1 mmol) was added dropwise to a vigorously stirred solution of H3p (233 mg, 0.50 mmol) in methanol (10 mL). A white precipitate rapidly appeared. The mixture was stirred for 30 min and then cooled down in an ice bath. The white solid that precipitated was then filtered, washed with methanol and dichloromethane and dried under vacuum. (328 mg, 0.39 mmol, 77%). FT-IR (KBr): ṽ, 3223, 2933, 2878 and 1383 cm^{-1}. $C_{28}H_{46}N_8O_6Zn_2$·4/3CH_3OH (888.2): calcd. C 39.67, H 5.83, N 15.77; found C 39.84, H 5.86, N 15.73. ^{1}H NMR (200 MHz, D_2O, 25 °C): δ = 1.40−2.00 (m, 8 H, $CH_2CH_2CH_2$), 2.86 (s, 16 H, NCH_2), 3.31 (s, CH_3OH) 3.97 (s, 5 H, $ArCH_2$), 3.77 (s, 3 H, $ArCH_2$), 7.41 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, D_2O, 25 °C): δ = 22.9 (NCH_2) 44.7, 45.4 ($CH_2CH_2CH_2$), 49.5 (CH_3OH), 50.7 ($ArCH_2$) 129.9 (arom. tert.), 133.9, 136.1 (arom. quat.) ppm. MS: *m*/*z* = 783.66 [$Zn_2(NO_3)_3$(H3p)], 656.19 [$Zn(NO_3)_2$(H3p)], 594.19 [$Zn(NO_3)$(H3p)].

[Zn_2Cl_4(H3p)]·7/3H_2O (4·7/3H_2O): A methanol (5 mL) solution of $ZnCl_2$ (27 mg, 0.20 mmol) was added dropwise to a vigorously stirred solution of H3p (47 mg, 0.10 mmol) in methanol (3 mL). A white precipitate rapidly appeared. The mixture was stirred for 2 h and then cooled down in an ice bath. The white solid that precipitated was then filtered, washed with methanol and dried under vacuum. (25 mg, 0.34 mmol, 34%). FT-IR (KBr): ṽ, 3212, 2933, 2874 and 1431 cm^{-1}. $C_{28}H_{46}N_6Zn_2Cl_4$·7/3H_2O (781.3): calcd. C 43.04, H 6.54, N 10.76; found C 43.01, H 6.59, N 10.80. ^{1}H NMR (200 MHz, D_2O, 25 °C): δ = 1.74 (m, 8 H, $CH_2CH_2CH_2$), 2.89 (m, 16 H, NCH_2), 3.96 (s, 5 H, $ArCH_2$), 3.80 (s, 3 H, $ArCH_2$), 7.46 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, D_2O, 25 °C): δ = 22.2 ($CH_2CH_2CH_2$), 43.2, 43.9 (NCH_2), 50.5 ($ArCH_2$), 128.0, 128.2 (arom. tert.), 132.4, 133.5, 134.3 (arom. quat.) ppm. MS: *m*/*z* = 704.01 [Zn_2Cl_3(H3p)], 603.09 [$ZnCl_2$(H3p)], 567.64 [ZnCl(H3p)].

[Zn_2Cl_4(Me2p)] (5): Me2p (50 mg, 0.10 mmol) was dissolved in MeOH (2 mL). A solution of $ZnCl_2$ (28 mg, 0.20 mmol) dissolved in acetone (2 mL) was added to this solution. A white solid rapidly precipitated. The mixture was stirred for 30 min and the white solid filtered. The solid was collected and dissolved in CH_2Cl_2 (3 mL), filtered through celite and the solvent removed under vacuum. The residue that remained was washed with acetone and methanol to obtain the product as a white solid (56 mg, 0.07 mmol, 72%). FT-IR (KBr): ṽ = 1467 cm^{-1}. $C_{30}H_{50}Cl_4N_6Zn_2$ (767.3): calcd. C 46.96, H 6.57, N 10.95; found C 46.84, H 6.82, N 10.75. ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 2.41 (s., 12 H, NCH_3), 2.50−3.10 (m, broad, 22 H, NCH_2 and NCH_3), 3.78 (s, 8 H, $ArCH_2$), 7.39 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, CD_2Cl_2, 25 °C): δ = 32.7, 44.9, 43.3 (NCH_3), 56.0 (NCH_2), 63.7 ($ArCH_2$), 131.2 (arom. tert.), 135.7 (arom. quat.) ppm. ^{1}H NMR (200 MHz, D_2O, 25 °C,): δ = 1.98 (s, 6 H, NCH_3), 2.68 (s, 12 H, NCH_3), 2.85 (m, 8 H, NCH_2), 2.99 (m, 8 H, NCH_2), 3.99 (s, 8 H, $ArCH_2$), 7.56 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, D_2O, 25 °C): δ = 42.0, 43.9, (NCH_3), 53.7, 54.4, (NCH_2), 63.0 ($ArCH_2$), 134.1 (arom. tert.), 136.4 (arom. quat.) ppm. MS: *m*/*z* = 631.14 [$ZnCl_2$(Me2p)], 595.69 [ZnCl(Me2p)].

[Zn_2Cl_4(Me2m)]·2H_2O·CH_3OH (6·2H_2O·CH_3OH): Me2m (78 mg, 0.16 mmol) was dissolved in MeOH (2 mL), and $ZnCl_2$ (43 mg, 0.32 mmol) dissolved in MeOH (2 mL) was added. A white precipi-

tate rapidly appeared which redissolved upon stirring. The solvent was removed under vacuum and the residue was then dissolved in warm MeOH (5 mL). Upon standing, the product crystallised as white blocks (81 mg, 0.11 mmol, 67%). FT-IR (KBr): $\tilde{\nu}$, 1467 cm^{-1}. $C_{30}H_{50}N_6Zn_2Cl_4 \cdot 2H_2O \cdot CH_3OH$ (835.4): calcd. C 44.57, H 7.00, N 10.06; found C 44.44, H 6.89, N 10.23. ^1H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 2.32 (s, 12 H, NCH_3), 2.41 (s, 9 H, NCH_3 and DMSO) 2.50−2.571 (m, 16 H, NCH_2), 3.43 (s, CH_3OH), 3.77 (s, 8 H, $ArCH_2$), 4.16 (s, broad, OH), 7.38 (m, 6 H, arom.), 7.77 (s, broad, 2 H, arom.) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 42.8, 43.4 (NCH_3), 48.7 (CH_3OH), 53.3, 54.7 (NCH_2), 60.3 ($ArCH_2$), 127.8, 129.1 (arom. tert.), 136.4 (arom. quat.).

[Zn_2Cl_4(Me3p)]·1/3CH_2Cl_2 (7·1/3CH_2Cl_2): Me3p (65 mg, 0.12 mmol) was dissolved in MeOH/CH_2Cl_2 (2:1 v:v; 3 mL) and a solution of $ZnCl_2$ (32 mg, 0.24 mmol) in MeOH (3 mL) was added. A white precipitate rapidly appeared which was filtered, collected and dried under vacuum (65 mg, 0.08 mmol, 67%). FT-IR (KBr): $\tilde{\nu}$ = 1467 cm^{-1}. $C_{34}H_{58}Cl_4N_6Zn_2 \cdot 1.5CH_2Cl_2$ (950.8): calcd. C 44.84, H 6.47, N 8.84; found C 44.59, H 6.67, N 8.61. ^1H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 1.67 (m, 8 H, $CH_2CH_2CH_2$), 2.18 (s, 12 H, NCH_3), 2.28 (s, 6 H, NCH_3), 2.70−2.30 (m, 16 H, NCH_2), 3.46 (s, 8 H, $ArCH_2$), 7.24 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 23.3 ($CH_2CH_2CH_2$), 42.2 (NCH_3), 55.0, 55.2 (NCH_2 and CH_2Cl_2), 61.5, 79.6 ($ArCH_2$), 129.1 (arom. tert.),137.5 (arom. quat.) ppm. ^1H NMR (200 MHz, D_2O, 25 °C): δ = 1.89 (m., 8 H, $CH_2CH_2CH_2$), 2.53 (s, 12 H, NCH_3), 2.53 (s, 6 H, NCH_3), 2.83, (m, 16 H, NCH_2), 3.91 (s, 8 H, $ArCH_2$), 7.47 (s, 8 H, arom.) ppm. ^{13}C NMR (50 MHz, D_2O, 25 °C): δ = 23.4 ($CH_2CH_2CH_2$), 43.4 (NCH_3), 56.2, 56.9 (NCH_2), 62.8 ($ArCH_2$), 133.7 (arom. tert.), 136.8 (arom. quat.) ppm. MS: *m*/*z* = 687.25 [$ZnCl_2$(Me3p)], 651.80 [ZnCl(Me3p)].

[Zn_2Cl_4(Me3m)]·H_2O (8·H_2O): Me3m (142 mg, 0.26 mmol) was dissolved in MeOH (3 mL). $ZnCl_2$ (71 mg, 0.52 mmol) dissolved in MeOH (1 mL) was added to this solution. The solution was vigorously stirred until a fine white powder precipitated. The solid was filtered, collected and dried under vacuum (125 mg, 0.15 mmol, 59%). The product was recrystallised from $CHCl_3$ to obtain a white microcrystalline solid insoluble in most common solvents (42 mg, 0.05 mmol, 19.8%). FT-IR (KBr): $\tilde{\nu}$ = 1467 cm^{-1}. $C_{34}H_{58}Cl_4N_6Zn_2 \cdot H_2O$ (841.5): calcd. C 48.53, H 7.19, N 9.99; found C 48.61, H 6.85, N 9.94.

Kinetics of *p*-Nitrophenyl Acetate (NA) Hydrolysis: The hydrolysis rate of NA in the presence of the Zn complexes was measured in a H_2O/CH_3CN (90:10 v:v) solution by an initial-slope method, following the increase in the 402 nm absorption of the released *p*-nitrophenolate at 298 K (± 0.05 K). The molar absorbance of *p*-nitrophenolate was determined at the pH of each measurement. The qionic strength was adjusted to 0.1 with $NaNO_3$. pH was adjusted with Tris buffer (pH 7−9; 50 mM). In a typical experiment, after mixing NA (5.15×10^{-4} M) and the Zn complex (0.1−0.5 mM) in 10% CH_3CN solution at appropriate pH (the reference experiment uses only the Zn^{II} complex), the UV absorption decay was recorded immediately and was followed generally until 2% decay of NA. This provided v_{in} values from which pseudo-first-order rate constants, k_{in}, calculated according to the expression $k_{in} = v_{in}/[NA]$. Second-order rate constants, k_{NA}, were obtained at a given pH from the plot of k_{in} vs. complex concentration.

X-ray Crystallography: Single crystals of $[Zn_2(NO_3)_2(H3p)](NO_3)_2$ (**3**) suitable for X-ray analysis were obtained from a concentrated methanol solution of the complex upon standing. Suitable crystals of [Zn_2Cl_4(Me2p)] (**5**) were obtained as colourless plates by slow evaporation of a CD_2Cl_2 solution. Suitable crystals of [Zn_2Cl_4(Me3p)]·1/3CH_2Cl_2 (**7·1/3CH_2Cl_2**) were obtained as colourless blocks by slow evaporation of a CH_3OH/CH_2Cl_2 (1:1 v:v) solution. Suitable crystals of [Zn_2Cl_4(Me3m)] (**8**) were obtained as colourless blocks by recrystallisation of the crude reaction mixture from a $CHCl_3$/MeOH/benzene/THF (2:1:1:1 v:v) mixture.

For **3**, data were collected on a Bruker Smart CCD diffractometer, using Mo-K_α (λ = 0.71073 Å) radiation. A summary of the fundamental crystal data and refinement data are given in Table 1. Data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Cell parameters were determined and refined by a least-squares fit of all reflections collected (θ range = 2.33 to 25°, *hkl* from −16, −17, −19 to 13, 18, 19, respectively). Each frame exposure time was of 20 s, covering 0.3° in ω. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. No appreciable decay in the intensities of standard reflections was observed. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXS-97).[32] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms, with exceptions. For the NO_3^- counteranion, no resolvable positional disorder of these atoms was found, and they were isotropically refined. Hydrogen atoms were included in calculated positions and refined as riding on the respective carbon atoms, with the thermal parameters related to the bonded atoms, except H1, H2 and H3, bonded to nitrogen atoms, which were located in a Fourier synthesis, included and their parameters fixed. The largest residual peaks in the final difference map, maximum 1.052 e·$Å^{-3}$, are close to the non-coordinating NO_3^- anion.

The intensity data were collected at 298 K (**8**) or 223 K (**5** and **7·1/3CH_2Cl_2**) on a Stoe Image Plate Diffraction System[33] using Mo-K_α (λ = 0.71073 Å) graphite-monochromated radiation. Image plate distance: 70 mm; φ oscillation scans: 0−200°; step Δφ: 1.0°; 2θ range: 3.27−52.1°; $d_{max}-d_{min}$ = 12.45−0.81 Å. The structures were solved by direct methods using the program SHELXS-97.[34] The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The refinement and all further calculations were carried out using SHELXL-97.[34] The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. For **7·1/3CH_2Cl_2** a small amount of residual electron density was located in a final difference Fourier synthesis at the origin of the unit cell about a threefold inversion axis. The SQUEEZE routine in PLATON[35] indicated the presence of a solvent accessible region of ca. 100 electrons for a volume of 1507 $Å^3$. This was equated to be equal to one third (1/3) of a highly disordered CH_2Cl_2 molecule per molecule of complex, and the HKL file was modified accordingly. The molecular structure and crystallographic numbering scheme are illustrated in the ORTEP drawing (Figure 1).

Crystallographic data for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-212656 ... -212659, for the complexes **3**, **5**, **7·1/3** CH_2Cl_2 and **8**, respectively. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Supporting Information Available: NMR spectral characterisation data for the complexes described in the present work and VT-^1H NMR spectra of **5**. Kinetic data for the hydrolytic reactions.

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