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Zinc(II) complexes derived from potentially hexadentate (N_4O_2) acyclic ligands containing pyridinyl and phenolic groups

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A group of zinc(II) complexes derived from potentially hexadentate (N_4O_2) acyclic ligands derived from Schiff bases and bearing pyridinyl and phenolic arms have been prepared and characterized. The crystal structures of two of them show that hydrolysis of the corresponding pro-ligand has occurred to give mononuclear zinc complexes. The co-ordination geometries around the zinc are approximately trigonal biopyramidal.

Zinc(II) is present at the active sites of various enzymes in living systems and plays a central role in catalysis and gene expression.[1–5] In enzymes with hydrolytic activity towards phosphate esters[5,6] the active zinc centre usually displays a tetrahedral or distorted-tetrahedral co-ordination geometry in which one site is occupied by a water molecule.[5,7] During the course of enzymatic turnover, the inner-sphere co-ordination number of catalytic zinc may increase to five with accompanying change of geometry to either trigonal bipyramidal or 'octahedral-minus-one'. In (aqueous) solution, and in small-molecule complexes, species containing zinc(II) with co-ordination number six are common.[8,9] It is the flexibility of co-ordination number and co-ordination polyhedra that may enable zinc(II) to reveal its essential catalytic function as during a reaction this will enable a substrate to bind to the metal without releasing another group from the co-ordination sphere.[8]

In order to elucidate the mechanism of zinc(II) involvement in hydrolytic enzymes, small-molecule zinc complexes have been synthesized as models for the active site and their properties investigated.[10–15] In these models relatively rigid ligands providing three or four donor sites were used as such ligands leave zinc(II) co-ordinatively unsaturated and so enable co-ordination of the water that is believed to play an essential role in hydrolysis. In addition, phosphate-bridged dinuclear zinc complexes[16] and a phenoxy-bridged homodinuclear zinc complex,[17] related to the dinuclear component in some multizinc enzymes, have been reported. Herein we report the synthesis of a series of mononuclear zinc(II) complexes, with different co-ordination numbers, derived from acyclic and potentially hexadentate (N_4O_2) ligands containing pyridinyl and phenolic groups, together with the crystal structures of two complexes which result from hydrolytic cleavage of the precursor di-Schiff base pro-ligand.

Experimental

Reagents and solvents used were of commercial reagent quality. Purification of the pro-ligands was effected by using flash chromatography[18] with silica gel (40–63 μm). Their identity and purity was judged by TLC, ^{1}H NMR, and mass spectroscopy. All elemental analyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1710 Fourier-transform spectrophotometer (4000–400 cm^{-1}), electronic absorption spectra using a Philips PU8720 UV/VIS scanning spectrophotometer operating in the range 220–500 nm, ^{1}H NMR spectra at 220 MHz on a Perkin-Elmer R34 spectrometer and ^{13}C NMR spectra (62.9 MHz) using a Bruker AM-250 spectrometer. Positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Kratos Ms 80 spectrometer. The matrix used was 3-nitrobenzyl alcohol unless otherwise stated. All solid samples prepared were dried in vacuum over silica gel and $MgSO_4$ overnight unless otherwise stated.

CAUTION: although no problems were encountered during the preparation of the perchlorate salts and the use of perchloric acid in titration, suitable care and precautions should be taken when handling such potentially hazardous compounds.

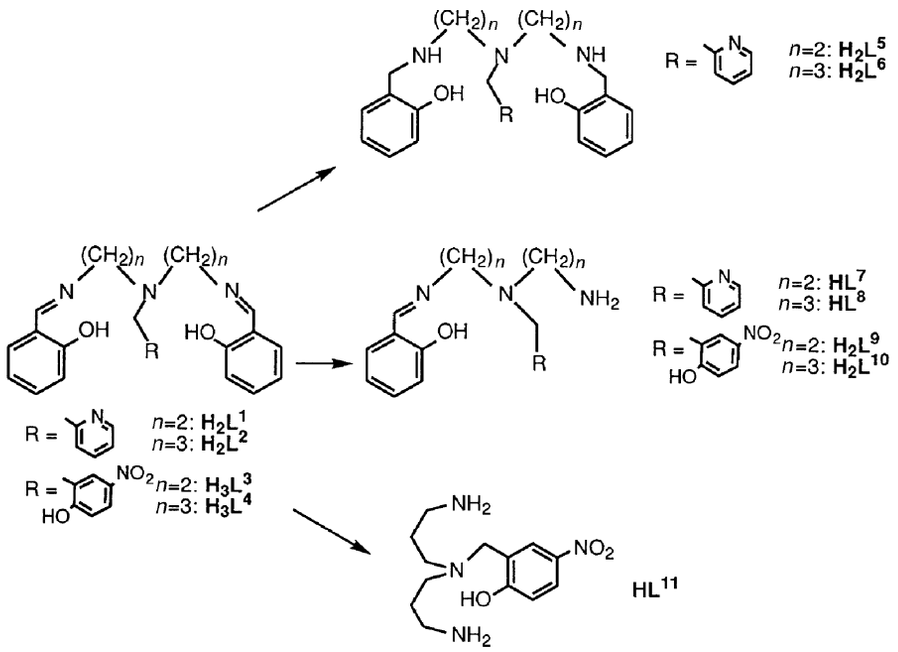
Preparation of pro-ligands

The pro-ligands are shown in scheme 1.

The compounds H_2L^1 and H_2L^2 were prepared as described previously.[19]

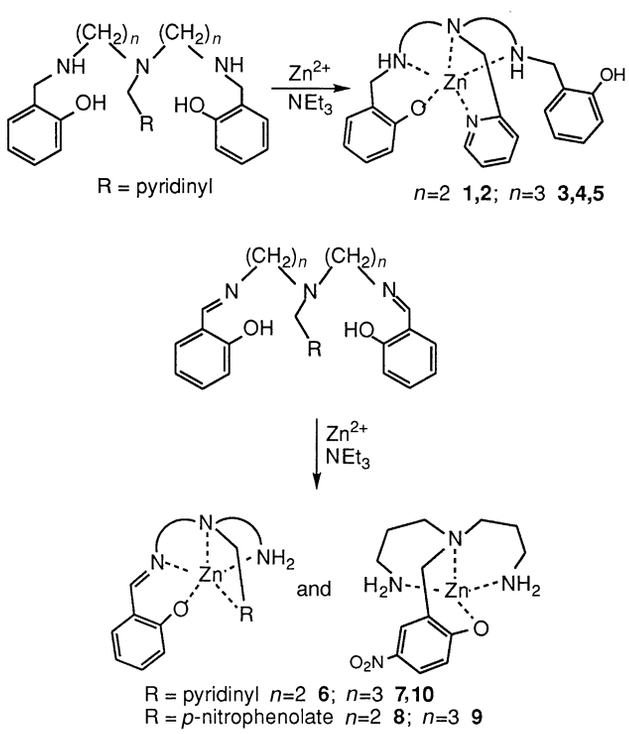
H_3L^3. An ethanolic solution (10 cm^3) containing diethylenetriamine hydrochloride (5 mmol; 1.74 g) was added dropwise to a tetrahydrofuran (thf) solution (60 cm^3) containing 2-chloromethyl-4-nitrophenol (5 mmol, 0.94 g) while stirring and then NEt_3 (20 mmol, 2.02 g) was added. The mixture was heated to reflux for 2 h. After cooling, the resulting suspension was filtered to remove solid NEt_3·HCl. The filtrate was evaporated to produce an oily syrup. This was dissolved in CH_2Cl_2–MeOH (9:1) and chromatographed using a silica gel column to yield H_3L^3 (1.30 g, 56.4%). NMR ($CDCl_3$): ^{1}H, δ 12.35 (s, 1 H), 8.30 (s, 2 H), 8.05 (d, 1 H), 7.95 (s, 1 H), 7.35–6.70 (m, 9 H), 4.00 (s, 2 H), 3.75 (t, 4 H) and 3.00 (t, 4 H); ^{13}C, δ 55.21, 57.15, 58.15, 115.20, 116.93, 118.53, 118.83, 121.66, 124.71, 125.60, 131.69, 132.56, 140.30, 160.76, 164.04 and 167.05. Mass spectrum: *m/z* 463 (M^+, 100%).

H_3L^4. 3,3′-Iminobis(propylamine) (12.5 mmol, 1.64 g) and salicylaldehyde (25 mmol, 3.05 g) were stirred together in absolute ethanol at room temperature for 30 min and then 2-chloromethyl-4-nitrophenol (12.5 mmol, 2.35 g; in 50 cm^3 EtOH) and Na_2CO_3 (15 mmol, 1.6 g) were added to the yellow solution. The mixture was heated to reflux overnight. On cooling, the resulting suspension was filtered and the filtrate evaporated to remove solvent. Methanol (20 cm^3) was added to the syrupy residue and the mixture heated. The resulting solution was allowed to stand at room temperature overnight and a yellow solid deposited. Recrystallization of the solid from MeOH (65 cm^3) gave H_3L^4 as a yellow microcrystalline powder (4.62 g, 75.4%) (Found: C, 65.8; H, 6.0; N, 11.3. Calc. for $C_{27}H_{30}N_4O_5$: C, 66.1; H, 6.15; N, 11.4%). NMR ($CDCl_3$): δ 8.30 (s, 2 H), 8.05 (d, 1 H), 7.90 (s, 1 H), 7.25 (m, 4 H), 6.85 (m, 5 H), 3.90 (s, 2 H), 3.60 (t, 4 H), 2.70 (t, 4 H) and 2.00 (m, 4 H); ^{13}C, δ 27.32, 51.08, 56.99, 57.67, 116.50, 116.97, 118.57, 118.71, 121.59, 124.61, 125.40, 131.33, 132.41, 140.15, 160.94, 164.49 and 165.72. IR (cm^{-1}): 1636 (C=N). Mass spectrum: *m/z* 490 (M^+, 100%).



Scheme 1

H_2L^5 and H_2L^6. The Schiff-base precursor H_2L^1 (0.40 g) or H_2L^2 (0.43 g) (1 mmol) was dissolved in 95% EtOH (75 cm^3) to which solution $NaBH_4$ powder (10 mmol, 0.38 g) was added in small portions. The mixture was stirred at room temperature for 2 h. 2 mol dm^{-3} Hydrochloric acid was added dropwise until pH ≈ 8 and stirring was continued for 30 min. The resulting suspension was filtered to remove any white solid and the filtrate evaporated to dryness. The residue was extracted with CH_2Cl_2–water and the CH_2Cl_2 removed to leave a straw-yellow oil (H_2L^5, H_2L^6). The oil H_2L^5 was dissolved in $CHCl_3$ (5 cm^3) and allowed to stand at −20 °C for a few days, when clear needle crystals were deposited; under the same conditions H_2L^6 remained as an oil. H_2L^5: ^{1}H NMR ($CDCl_3$) δ 2.62 (m, 8 H, Et), 3.75 (s, 2 H, CH_2), 3.86 (s, 4 H, CH_2), 5.72 (br, 2 H, NH), 6.70–7.52 (m, 11 H, aryl) and 8.40 (d, 1 H, H^6 of pyridyl); ^{13}C NMR ($CDCl_3$) δ 48.8, 52.8, 53.4, 60.0, 116.3, 118.9, 122.2, 122.3, 123.2, 128.6, 128.7, 136.7, 149.3, 157.6 and 158.4; mass spectrum m/z = 407 ($M + H^+$, 100%); accurate mass found (required) 407.244 809 (407.244 702). H_2L^6: ^{1}H NMR ($CDCl_3$) δ 1.40 (m, 4 H, CH_2), 2.25 (t, 4 H, CH_2), 2.45 (t, 4 H, CH_2), 3.40 (s, 2 H, CH_2), 3.70 (s, 4 H, CH_2), 5.00 (br, 2 H, NH), 6.5–7.30 (m, 11 H, aryl), 8.00 (d, 1 H, H^6 of pyridyl); ^{13}C NMR ($CDCl_3$) δ 26.2, 47.3, 52.3, 52.6, 60.0, 116.4, 118.9, 122.2, 122.4, 123.2, 128.5, 128.7, 136.6, 149.1, 158.3 and 159.1; mass spectrum m/z = 435 ($M + H^+$, 100%); accurate mass found (required) 435.276 882 (435.276 002).



Scheme 2

Preparation of complexes

The ligand frameworks for the complexes are depicted in Scheme 2.

[Zn(HL^5)]ClO_4·$MeCO_2Et$·0.5H_2O 1. Pro-ligand H_2L^5 (1 mmol, 0.41 g) and NEt_3 (2 mmol, 0.20 g) were dissolved in MeOH (50 cm^3) and $Zn(ClO_4)_2$·$6H_2O$ (1.5 mmol, 0.55 g) in MeOH (5 cm^3) was added. The solution was heated to reflux for 3 h. On cooling, the resulting mixture was filtered and the filtrate evaporated to near dryness. Methanol (5 cm^3) and then ethyl acetate (40 cm^3) were added to dissolve the residue, the solution was warmed and then allowed to stand at room temperature overnight, white small crystals deposited. Recrystallization of the product from MeCN–MeOH gave crystals that are unstable in the atmosphere. Yield = 0.38 g, 59%. IR (KBr disc, $\tilde{\nu}/cm^{-1}$): 3422 (H_2O), 3244 (OH), 2928 and 2879 (NH), 1727 ($MeCO_2Et$), 1112 and 623 (ClO_4). Mass spectrum: m/z = 469 (M^+, 100%) [Found (required for $C_{28}H_{38}ClN_4O_{8.5}Zn$): C, 50.35 (50.5); H, 5.75 (5.75); N, 8.5 (8.4%)].

[Zn(HL^5)]BF_4·$MeCO_2Et$ 2. This was prepared from $Zn(BF_4)_2$·H_2O (1.5 mmol, 0.36 g) using the same procedure as for complex **1**. The product is microcrystalline. Yield = 0.42 g, 64%. IR (KBr disc, $\tilde{\nu}/cm^{-1}$): 3286 (OH), 2916 and 2868 (NH), 1736 ($MeCO_2Et$) and 1083 (BF_4). Mass spectrum: m/z = 469 (M^+, 100%) [Found (required for $C_{28}H_{37}BF_4N_4O_4Zn$): C, 52.3 (52.15); H, 5.65 (5.8); N, 8.75 (8.7%)].

[Zn(HL^6)]BF_4 3. This was prepared from H_2L^6 (1 mmol, 0.44 g) and $Zn(BF_4)_2$·H_2O using the same procedure. White needle-like crystals were generated. Yield = 0.32 g, 46%. IR (KBr disc, $\tilde{\nu}/cm^{-1}$): 3260 (OH), 3060, 2926 and 2879 (NH) and 1083 (BF_4).

Table 1 Crystallographic data for complexes **6** and **8**

	6	**8**
Formula	$C_{41}H_{41}BN_4OZn$	$C_{19}H_{24}N_4O_5Zn$
M	681.96	453.80
Crystal symmetry	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	10.332(5)	10.285(6)
b/Å	23.057(6)	10.364(7)
c/Å	14.773(7)	10.619(6)
α/°		68.17(4)
β/°	94.08(5)	82.69(4)
γ/°		71.34(5)
U/Å^3	3510(3)	995(1)
F(000)	1432	469.89
Z	4	2
μ(Mo-Kα)/cm^{-1}	7.38	12.99
Crystal size/mm	0.75 × 0.45 × 0.15	1.0 × 0.85 × 0.575
D_c/g cm^{-3}	1.290	1.761
λ(Mo-Kα)/Å	0.710 73	0.710 69
T/K	293(2)	295
No. of reflections	5621	3531
Independent reflections	4305	2218
Final R	0.0405	0.0652

Mass spectrum: $m/z = 497$ (M^+, 100%) [Found (required for $C_{26}H_{33}BF_4N_4O_2Zn$): C, 53.1 (53.4); H, 5.7 (5.7); N, 9.4 (9.55%)].

[Zn(HL^6)]ClO$_4$·MeCO$_2$Et 4. This was prepared from H_2L^6 (1 mmol, 0.44 g) using the same procedure. White microcrystals were generated. Yield = 0.37 g, 53%. IR (KBr disc, $\tilde{\nu}$/cm^{-1}): 3222 (OH), 2934 and 2865 (NH), 1726 ($MeCO_2Et$), 1108 and 623 (ClO_4). Mass spectrum: $m/z = 497$ (M^+, 100%) [Found (required for $C_{30}H_{41}ClN_4O_8Zn$): C, 52.55 (52.6); H, 6.0 (6.05); N, 7.95 (8.2%)].

[Zn(HL^6)]BPh$_4$·H$_2$O 5. This was prepared from equal molar amounts of H_2L^6 (1 mmol, 0.44 g) and $Zn(BF_4)_2·H_2O$ (0.24 g) in EtOH (30 cm^3) with a similar procedure to that used for complex **1**. After treatment with sodium tetraphenylborate at reflux temperature for 2 h the resulting yellow-white solid was recrystallized from EtOH (50 cm^3). Yield = 0.53 g, 63%. IR (KBr disc, $\tilde{\nu}$/cm^{-1}): 3496 (OH), 2998, 2865 (NH), 766, 732 and 708 (BPh_4). Mass spectrum: $m/z = 497$ (M^+, 100%) [Found (required for $C_{50}H_{55}BN_4O_3Zn$): C, 71.85 (71.8); H, 6.8 (6.65); N, 6.9 (6.7%)].

[ZnL^7]BPh$_4$ 6. Equimolar amounts of H_2L^1 (1 mmol, 0.40 g) and $Zn(ClO_4)_2·6H_2O$ (0.37 g) in MeOH (50 cm^3) were heated to reflux in the presence of NEt_3 (2 mmol, 0.20 g) for 1 h. Sodium tetraphenylborate (1 mmol, 0.34 g in 5 cm^3 MeOH) was added. The clear solution was refluxed for half an hour, a white solid emerging after a few minutes. The resulting suspension was filtered and a yellow-white crystalline powder was recovered from the filtrate on cooling (0.55 g, 82%). Recrystallization of the powder from MeOH–MeCN (1:1) gave light yellow crystals suitable for X-ray analysis (Found: C, 72.3; H, 6.3; N, 8.5. Calc. for $C_{41}H_{41}BN_4OZn$: C, 72.2; H, 6.05; N, 8.2%). IR (cm^{-1}): 1632 (C=N). Mass spectrum: m/z 361 (M^+, 100%).

[ZnL^8]BPh$_4$ 7. The complex was prepared similarly to **6** using H_2L^2 (1 mmol, 0.43 g). A white crystalline solid was collected (0.5 g, 76%) (Found: C, 72.45; H, 6.5; N, 7.5. Calc. for $C_{43}H_{45}BN_4OZn$: C, 72.75; H, 6.4; N, 7.9%). IR (cm^{-1}): 1619 (C=N). Mass spectrum: m/z 389 (M^+, 100%).

[ZnL^9]·MeOH 8. The compound H_3L^3 (1 mmol, 0.46 g) and $Zn(ClO_4)_2·4$dmso (dmso = dimethyl sulfoxide) (1.5 mmol, 0.52 g) in MeOH (50 cm^3) were stirred and then NEt_3 (3 mmol, 0.30 g) was added. The mixture was heated to reflux for 2 h. On cooling, the resulting solution was filtered to remove residual solids. The filtrate was allowed to stand at room temperature overnight and yellow prismatic crystals suitable for X-ray analysis were deposited (0.24 g, 53%) (Found: C, 50.5; H, 5.3; N, 12.0. Calc. for $C_{19}H_{24}N_4O_5Zn$: C, 50.3; H, 5.35; N, 12.35%). IR (cm^{-1}): 1637 (C=N) and 1294 (NO_2). Mass spectrum: m/z 421 (M^+, 100%).

[ZnL^{10}] 9 and [ZnL^{11}]ClO$_4$·MeOH 10. A methanolic solution (55 cm^3) containing ligand H_3L^4 (1 mmol, 0.49 g) and $Zn(ClO_4)_2·6H_2O$ (1.5 mmol, 0.56 g) was stirred and NEt_3 (3 mmol, 0.30 g) added with immediate production of a yellow precipitate. The suspension was heated to reflux for 2 h. On cooling, the resulting mixture was filtered to obtain a yellow powder that was recrystallized from MeCN–MeOH (1:1) to give complex **9** (0.22 g, 48%) (Found: C, 53.1; H, 5.25; N, 12.15. Calc. for $C_{20}H_{24}N_4O_4Zn$: C, 53.4; H, 5.4; N, 12.45%). IR (cm^{-1}): 1628 (C=N) and 1293 (NO_2). Mass spectrum: m/z 449 (M^+, 89%). The filtrate was allowed to stand at room temperature for a few days during which time complex **10** was deposited as light yellow crystals (0.09 g, 21%) (Found: C, 35.2; H, 5.0; N, 12.15. Calc. for $C_{14}H_{25}ClN_4O_8Zn$: C, 35.15; H, 5.25; N, 11.7%). IR (cm^{-1}): 1293 (NO_2) and 1097 (ClO_4^-). Mass spectrum: m/z 345 (M^+, 100%).

Crystallography

Complex 6. A yellow crystal having dimensions of 0.75 × 0.45 × 0.15 mm was used to collect X-ray data at room temperature in the range $3.5 < 2\theta < 45.0°$ on a Siemens P4 diffractometer by the ω-scan method (h −1 to 11, k −1 to 24, l −15 to 15). Of the 5621 reflections measured the 4305 independent reflections with $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz-polarization effects and for absorption based upon symmetry-equivalent reflections (maximum and minimum transmission coefficients 0.397 and 0.302). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode with isotropic thermal vibrational parameters related to those of the supporting atoms. Refinement converged at a final $R = 0.0405$ ($wR2 = 0.1193$ for all 4299 unique data, 433 parameters, mean and maximum δ/σ 0.000, 0.001), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.226 and 0.256 e Å^{-3} close to the metal atom. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.20P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93[20] as implemented on a Viglen 486dx computer.

Complex 8. Three-dimensional room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50.0°$ on a Nicolet R3 four-circle diffractometer by the ω-scan method. The 2218 independent reflections (of 3531 measured) for which $|F|/\sigma(|F|) > 5.0$ were corrected for Lorentz-polarization effects, and for absorption by analysis of eight azimuthal scans (minimum and maximum transmission coefficients 0.598 and 0.449). The structure was solved by standard Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom and refined in riding model. Refinement converged at a final $R = 0.0652$ for 262 parameters with allowance for the thermal anisotropy of all non-hydrogen atoms (mean and maximum δ/σ 0.001 and 0.010). Minimum and maximum final electron density −0.588 and 1.040 e Å^{-3} located around the zinc atom. Complex scattering factors were taken from ref. 21 and from the program package SHELXTL[22] as implemented on a Data General DG30 computer.

Crystal data together with details of the X-ray diffraction experiments for the two complexes are summarized in Table 1.

Atomic coordinates, thermal parameters, and bond lengths

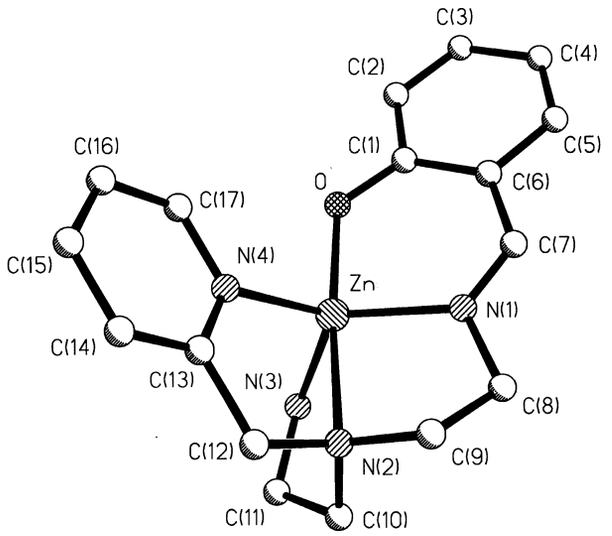


Fig. 1 Molecular geometry of the cation in complex **6**

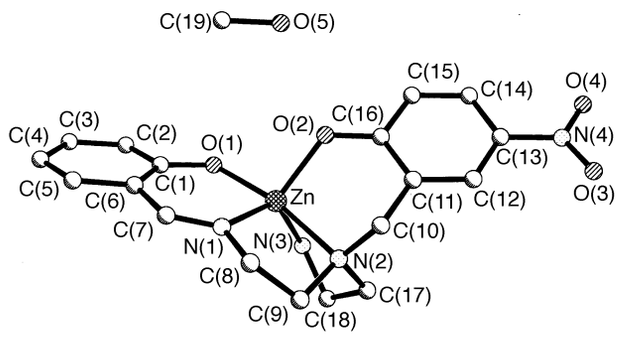


Fig. 2 Molecular geometry of complex **8**

and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/310.

Results and Discussion

Pro-ligands H_2L^5 and H_2L^6 were prepared by reduction of the corresponding Schiff-base ligand with $NaBH_4$ in ethanol. The absence of strong bands at 1635 cm^{-1} (characteristic of imine C=N bond stretches) and the presence of medium bands at 1600–1580 cm^{-1} (attributable to N–H bending modes), in the IR spectra, confirmed the successful *in situ* reduction. The mass spectra gave clear molecular ion $M + H^+$ peaks and accurate mass peaks at 407.244 809 for H_2L^5 and 435.276 882 for H_2L^6 were determined and compared to the calculated values of 407.244 702 and 435.276 002; the isotopic patterns of these peaks are consistent with the theoretical patterns.

The ^{1}H NMR spectra for the pro-ligands showed the presence of a singlet at $\delta \approx 3.90$ corresponding to the methylene protons introduced by reduction of the imine bonds and no imine-related proton singlet was observed. The ^{13}C NMR data also confirmed the successful reduction of imines as the carbon signals of imine C=N bonds at $\delta \approx 165$ were replaced by methylene carbon signals at $\delta \approx 52$ in the spectra of the reduced compounds.

When the reduced amine phenol pro-ligands were employed in complexation reactions with an excess amount of zinc(II) a series of mononuclear zinc(II) complexes [Zn(HL)X] were obtained. These are recovered as white-yellow microcrystals after crystallization from appropriate solvents; unfortunately crystals suitable for X-ray crystallography were not obtained. The zinc complexes are proposed to have similar structures to

Table 2 Selected bond lengths (Å) and angles (°) for complex **6**

Zn–O	1.961(3)	Zn–N(1)	2.009(3)
Zn–N(3)	2.030(3)	Zn–N(4)	2.042(3)
Zn–N(2)	2.313(3)		
O–Zn–N(1)	93.15(12)	O–Zn–N(3)	109.18(12)
N(1)–Zn–N(3)	118.55(13)	O–Zn–N(4)	99.64(11)
N(1)–Zn–N(4)	121.69(12)	N(3)–Zn–N(4)	110.13(12)
O–Zn–N(2)	169.35(10)	N(1)–Zn–N(2)	79.96(12)
N(3)–Zn–N(2)	81.34(11)	N(4)–Zn–N(2)	77.53(11)

Table 3 Selected bond lengths (Å) and angles (°) for complex **8**

Zn–O(1)	1.986(5)	Zn–O(2)	1.979(7)
Zn–N(1)	2.045(6)	Zn–N(2)	2.260(5)
Zn–N(3)	2.061(8)		
O(1)–Zn–O(2)	100.3(2)	O(1)–Zn–N(1)	91.1(2)
O(2)–Zn–N(1)	116.4(3)	O(1)–Zn–N(2)	168.6(2)
O(2)–Zn–N(2)	90.3(2)	N(1)–Zn–N(2)	80.5(2)
O(1)–Zn–N(3)	98.0(2)	O(2)–Zn–N(3)	112.4(3)
N(1)–Zn–N(3)	127.6(3)	N(2)–Zn–N(3)	81.3(2)

that of the copper(II) analogue $[Cu(HL^6)]BF_4$.[23] In this complex one of the phenols in the pro-ligand does not deprotonate and the metal is co-ordinated in a distorted trigonal-bipyramidal manner by the three amine nitrogen atoms, one pyridine nitrogen atom and an oxygen atom from the phenolate; the phenolic arm does not engage in co-ordination.

The IR spectra of these zinc(II) complexes are similar in pattern to those of the pro-ligands. There are small shifts in the characteristic bands with the most significant difference being a decrease in intensity of the secondary amine bands at 3240–2800 cm^{-1}. There is a sharp band at *ca.* 3260 cm^{-1} assignable to the single phenol OH. Solvent ethyl acetate in the complexes gives an absorption at *ca.* 1730 cm^{-1} and the anions ClO_4^-, BF_4^- and BPh_4^- have bands at 1110, 1083 and 732 cm^{-1}, respectively. Positive-ion fast-atom bombardment (FAB) mass spectra provide further evidence for complex formation. For complexes **1**, **2** and **3**–**5**, the molecular peak can be identified as $[Zn(HL)]^+$ at *m/z* 469 and 497 respectively and whilst for complexes **1** and **3**–**5** extremely small peaks are detected assignable to species such as $[Zn_2(HL)_2]$ and $[Zn_2(HL)_2]X$, probably arising from aggregation processes in the matrix used; no intense peaks corresponding to oligonuclear species are found.

Treatment of the Schiff-base imine pro-ligands with an equimolar, or excess, amount of $Zn(ClO_4)_2$ in methanol in the presence of triethylamine yielded the five-co-ordinate mononuclear zinc(II) complexes **6**–**9**. Hydrolytic cleavage of one imine bond in the pro-ligand has occurred and although it is not proven it is likely that under the conditions of the reaction an activated nucleophile (OH) has been generated at the metal and is responsible for the ensuing cleavage reaction. For H_3L^4 further hydrolysis occurred during the reaction leading to the formation of complex **10**. This situation is very different from that found in the reaction of the pro-ligands H_2L^1 and H_2L^2 with $Cu(ClO_4)_2$ and triethylamine. No hydrolytic cleavage occurs and trinuclear complexes are generated in which two ligand molecules share three copper(II) atoms.[19]

Structures of complexes 6 and 8

The two complexes are mononuclear, five-co-ordinate species that show similar approximately trigonal-bipyramidal (*TBPY*) geometries with *TBPY* components $\tau = 0.79$ (**6**) and 0.68 (**8**) respectively. For perfect square-pyramidal and trigonal-bipyramidal geometries the values of τ are zero and unity respectively, τ being an index of the degree of trigonality within the structural continuum between square-pyramidal and trigonal-bipyramidal geometries.[24] The molecular structures,

with atom labelling, are illustrated in Figs. 1 and 2; relevant bond lengths and angles with standard deviations in Tables 2 and 3.

Complex **6** consists of a complex cation and a tetraphenylborate anion and the asymmetric unit of **8** comprises the neutral zinc(II) species and a methanol solvent molecule. In each of the two complexes one of the two imine bonds in the parent ligand has hydrolysed on reaction with $Zn(ClO_4)_2$ and the resultant primary amine nitrogen is co-ordinated to the metal atom at an equatorial position of the distorted trigonal-bipyramidal geometry adopted; the tertiary amino-nitrogen atom occupies an axial position.

In complex **6** the second axial site is a deprotonated phenolic oxygen [N(1), N(3), N(4) plane, with Zn −0.366, O −2.301 and N(2) 1.945 Å out of plane], with Zn–N distances 2.009, 2.030 and 2.042 Å in the equatorial plane, significantly shorter than the Zn–N(2) amine distance of 2.313 Å at the axial position; Zn–O 1.961. The phenyl and the pyridyl rings are planar [root mean square (r.m.s.) deviations 0.003, 0.001 Å respectively]; deviations of ring substituent atoms from planarity are small [O 0.005, C(7) −0.056 and C(12) −0.024 Å]. The angle between the pyridine and phenyl rings is 55.7°. Torsion angles of NCCN fragments are +45.1 and +55.6° respectively. The primary amine does not engage in any hydrogen bonding; this is very different from complex **3** where the appearance of *p*-nitrophenol results in the formation of hydrogen bonds.

In complex **8** two phenolate oxygens occupy different geometric sites (one axial and one equatorial); N(1), N(3) and O(2) make up the plane [Zn 0.221, O(1) 2.199 and N(2) −2.023 Å out of plane], with two different Zn–N distances, two of 2.045, 2.061 Å in the equatorial plane and 2.26 Å in an axial position, and two almost equal Zn–O distances of 1.979 and 1.986 Å. The methanol solvent molecule is involved in hydrogen bonding to the phenolate oxygen [O(5) · · · O(2) 2.807, H(O5) · · · O(2) 1.807 Å]. It is worth noting that the formation of the hydrogen bond and the existence of the electron-withdrawing group (NO_2) at the *para* position does not weaken the Zn–O(2) bond. This bond is marginally shorter than the second more normal zinc–oxygen bond (1.986 Å) and is the shortest bond within the zinc co-ordination sphere. The apical bonds average 2.125 Å; the mean value for the basal ligation is 2.068 Å. The Zn–N(2) bond (2.260 Å) formed between the metal and tertiary nitrogen is the longest and significantly longer than the average Zn–N distances. This may be related to the induction of stress from the presence of the two five-membered rings. The bond angles at the zinc atom are further indicative of *TBPY* symmetry.

The phenyl rings in complex **8** are planar (r.m.s. deviations 0.019, 0.011 Å); deviations of oxygen and nitrogen substituent atoms from planarity are small (less than 0.053 Å), but the imine and amine C are 0.157 and −0.141 Å out of planarity. The nitro group is asymmetrically twisted by 8.4° from the plane of the phenyl ring. The angle between the phenyl rings is 35.3°. Torsion angles of both NCCN fragments are +53°. The zinc OCCCN (imine) chelate ring is approximately planar (r.m.s. deviation 0.024 Å) and inclined at 5.7° to the phenyl ring.

In addition to the hydrogen bonding involving the methanol solvent molecule in complex **8**, there is a pair of longer, symmetry-related hydrogen bonds between the primary amine nitrogens and the other phenolate oxygens of a centrosymmetrically related molecule [N(3) · · · O(1^{I}) 2.950, H(N3A) · · · O(1^{I}) 2.018 Å; I $1 - x, -y, -z$]. The second hydrogen atom of the amine nitrogen points approximately to a symmetry-related O(4) of the nitro group [N(3) · · · O(4^{II}) 3.130, H(N3B) · · · O(4^{II}) 2.612 Å; II $x, y, 1 + z$].

Hydrolysis of phosphates by complexes 6 and 8

It was proposed that only those rigid, tri- or tetra-dentate ligands that bind zinc ions firmly under alkaline conditions and for which the zinc complexes are co-ordinatively unsaturated and/or sterically open for phosphate substrate approach can catalyse the hydrolysis of phosphate esters.[12] To test whether flexible five-co-ordinate zinc complexes have the propensity for inducing catalytic hydrolysis of phosphate esters, preliminary kinetic studies for the two complexes **6** and **8**, for which the structures have been determined crystallographically, were conducted using the UV/VIS spectroscopic method of Koike and Kimura.[11,25] The observed rate constant for hydrolysis of tris(4-nitrophenyl) phosphate catalysed by complex **6** is 3.95×10^{-4} s^{-1} (based on a pseudo-first-order reaction) compared with 3.60×10^{-5} s^{-1} found in the absence of the complex [25 °C, *N*′-(2-hydroxyethyl)piperazine-*N*-ethanesulfonic acid (hepes) buffer (10 mmol, 90% v/v EtOH and pH 7.37); $I = 0.2$ mol dm^{-3} ($NaClO_4$)]. A small enhancement is also noted for hydrolysis of bis(4-nitrophenyl) phosphate hydrolysis where the observed rate constant is 2.69×10^{-7} s^{-1} compared with 6.73×10^{-8} s^{-1} in the absence of the complex [35 °C; hepes buffer (10 mmol, 90% v/v EtOH and pH 7.37); $I = 0.2$ mol dm^{-3} ($NaClO_4$)]. Further studies were hampered due to the emergence of a small precipitate at higher pH. Potentiometric titrations on solutions (90% v/v ethanol) of the pro-ligand (1.0 mmol dm^{-3}) and an equimolar amount of zinc perchlorate showed that the complex has essentially formed by pH 6.7, therefore at the concentrations and pH values employed in this study it is likely that the complex is fully formed and so the accelerations noted can be attributed to its influence. For complex **8** no obviously enhanced rates, even for tris(4-nitrophenyl) phosphate, were observed under the present experimental conditions.

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