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Multinuclear zinc(II) complexes with $\{Zn_6(\mu\text{-}O)_6(\mu_3\text{-}O)_2\}$- and $\{Zn_5(\mu\text{-}O)_3(\mu_3\text{-}O)_3\}$-cluster cores

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2-Ethoxy-6-(((2-hydroxyphenyl)imino)methyl)phenol, H_2**1**, reacts with zinc(II) chloride in basic conditions to give $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$. The electrospray mass spectrum of a MeOH solution of the bulk sample provides evidence for $\{Zn_n(\mathbf{1})_n\}$ species with $n = 2–5$, while the ^1H NMR spectrum of a $CDCl_3$ solution of the bulk sample indicates the presence of at least four species. Single crystals of $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$ and $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$ were obtained from the same solution of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ in CH_2Cl_2/MeOH. Structural determinations confirm that these compounds contain $\{Zn_6(\mu\text{-}O)_6(\mu_3\text{-}O)_2\}$- and $\{Zn_5(\mu\text{-}O)_3(\mu_3\text{-}O)_3\}$-cluster cores, respectively, revealing that the *O,O′,N,O″*-donor set in $[\mathbf{1}]^{2-}$ is suited to the assembly of relatively high nuclearity zinc(II)-containing clusters.

1. Introduction

The clustering of zinc ions supported by Zn–O–Zn bridges makes multinuclear zinc(II) complexes attractive precursors for zinc oxide-based inorganic materials [1], and of relevance to the latter is the assembly of multinuclear zinc(II) complexes using macrocyclic or salen-type ligands [2–10]. Schiff base compartmental ligands are a favourite choice for such reactions. Large macrocyclic ligands present multiple hard *O*-donors within a moderately flexible environment which promotes the assembly of clusters of zinc(II) ions [11] and the use of large, acyclic Schiff base ligands to capture multiple Zn^{2+} and other metal ions has recently been reviewed [12]. Functionalizing the Schiff base ligand with O-containing donor substituents is one way to direct the assembly of Zn_xO_y clusters. Here we show that such assemblies can be achieved using the relatively simple Schiff base ligand H_2**1** (Scheme 1). Although coordination of H_2**1** [13] to copper(II), nickel(II) [14] and tin(IV) [15] has been reported, the ligand remains little investigated, despite its trivial synthesis.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer; chemical shifts are referenced to residual solvent peaks (with respect to TMS = δ 0 ppm). Solution electronic absorption and emission spectra were recorded on an Agilent 8453 spectrophotometer or Shimadzu RF-5301 PC spectrofluorometer, respectively, and FT-IR spectra using a Shimadzu 8400S instrument with solid samples using a Golden Gate ATR accessory. Electrospray ionization (ESI) mass spectra were recorded using a Bruker esquire 3000^{plus} or Finnigan MAT LCQ mass spectrometer.

2.2. Ligand $H_2$1

A solution of 2-aminophenol (0.55 g, 5.0 mmol) in MeOH (10 cm^3) was added to a stirred solution of 3-ethoxy-2-hydroxybenzaldehyde (0.83 g, 5.0 mmol) in MeOH (20 cm^3) and the resulting orange–red solution was heated at reflux for 2 h, then cooled to room temperature. The orange precipitate that formed was collected by filtration, washed with MeOH (10 cm^3) and dried in vacuo. Compound H_2**1** was isolated as an orange powder (0.91 mg, 70%). ^1H NMR (500 MHz, acetone-d_6) δ /ppm: 13.33 (s, 1H, H^{OH}, see text), 8.92 (s, 1H, $H^{CH=N}$), 8.52 (s, 1H, H^{OH}, see text), 7.33 (dd, $J = 7.9$, 1.5 Hz, 1H, H^{B3}), 7.20 (dd, $J = 7.8$, 1.4 Hz, 1H, H^{A5}), 7.16 (ddd, $J = 8.1$, 7.4, 1.6 Hz, 1H, H^{B5}), 7.08 (dd, $J = 8.0$, 1.4 Hz, 1H, H^{A3}), 7.01 (dd, $J = 8.1$, 1.3 Hz, 1H, H^{B6}), 6.93 (m, 1H, H^{B4}), 6.87 (t, $J = 7.9$ Hz, 1H, H^{A4}), 4.11 (q, $J = 7.0$ Hz, 2H, H^{Et}), 1.39 (t, $J = 7.0$ Hz, 3H, H^{Et}). ^{13}C NMR (126 MHz, acetone-d_6): δ/ppm 163.7 ($C^{CH=N}$), 152.9 ($C^{A1/B1}$), 152.0 ($C^{A1/B1}$), 148.7 (C^{A2}), 137.0 (C^{B2}), 129.0 (C^{B5}), 125.1 (C^{A5}), 121.2 (C^{B4}), 121.0 (C^{A6}), 120.6 (C^{B3}), 119.2 (C^{A4}), 118.0 (C^{A3}), 117.4 (C^{B6}), 65.4 (C^{Et}), 15.4 (C^{Et}). IR (solid, cm^{-1}) 3000br, 1623s, 1596s, 1545m, 1494m, 1470m, 1360m, 1305w, 1278m, 1225s, 1184m, 1167s, 1119w, 1048w, 1000w, 904w, 882w, 738s, 727s. UV/VIS λ_{max}/nm (1.19×10^{-5} mol dm^{-3}, CH_2Cl_2) 236 (ε dm^3 mol^{-1} cm^{-1} 21100), 282 (13400), 350 (14000). ESI-MS

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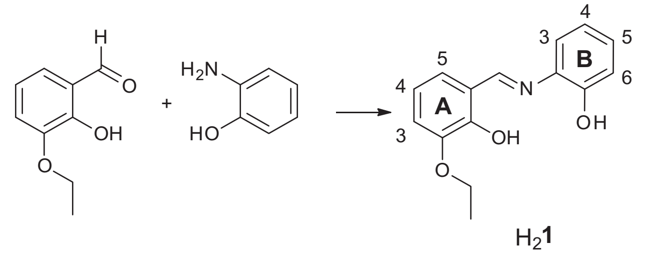

Scheme 1. Synthetic route to ligand H_2**1** with numbering scheme for the NMR assignments.

(MeOH) *m/z* 258.3 $[M+H]^+$ (calc. 258.1), 280.0 $[M+Na]^+$ (base peak, calc. 280.1), 537.1 $[2 M+Na]^+$ (calc. 537.2). Found: C, 70.01; H, 5.95; N; 5.36; $C_{15}H_{15}NO_3$ requires C 70.02, H 5.88, N 5.44%.

2.3. $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$

Anhydrous $ZnCl_2$ (0.134 g, 0.983 mmol) was added to a stirred solution of H_2**1** (0.129 g, 0.500 mmol) in CH_2Cl_2/MeOH (20 cm^3, 1:3, v/v), followed by the addition of LiOH (0.024 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 2 h, during which time a yellow precipitate formed. This was collected by filtration, was washed with MeOH (10 cm^3) and dried in vacuo. $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ was isolated as a yellow solid (52 mg, 0.033 mmol). Evaporation of a CH_2Cl_2/MeOH solution of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ over a month at room temperature yielded yellow crystals of $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$, and slow evaporation of the mother liquor gave further crystals of $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$ in addition to orange crystals of $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$ (see text). Bulk $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$: IR (solid, cm^{-1}): 3500w, 1607s, 1583s, 1550w, 1476s, 1460s, 1448s, 1385s, 1303s, 1282s, 1264s, 1250s, 1229s, 1183s, 1096w, 1016w, 910w, 874w, 843w, 823s, 735s. UV/VIS λ_{max}/nm (2.71×10^{-6} mol dm^{-3}, CH_2Cl_2) 237 (ε/$dm^3\ mol^{-1}\ cm^{-1}$ 102700), 310 (51600), 378 (53800), 417 (58200). ESI-MS (MeOH) *m/z* 643.2 $[Zn_2\mathbf{1}_2+H]^+$ (base peak, calc. 643.1), 665.2 $[Zn_2\mathbf{1}_2+Na]^+$ (calc. 665.0), 962.4 $[Zn_3\mathbf{1}_3+H]^+$ (calc. 962.1), 984.4 $[Zn_3\mathbf{1}_3+Na]^+$ (calc. 984.1), 1283.4 $[Zn_4\mathbf{1}_4+H]^+$ (calc. 1283.1), 1305.4 $[Zn_4\mathbf{1}_4+Na]^+$ (calc. 1305.1), 1602.3 $[Zn_5\mathbf{1}_5+H]^+$ (calc. 1602.1), 1624.3 $[Zn_5\mathbf{1}_5+Na]^+$ (calc. 1624.1). Found: C, 46.02; H, 3.71; N, 3.54; $C_{60}H_{58}Cl_2N_4O_{16}Zn_6$ requires C, 46.36; H, 3.76; N, 3.60%.

2.4. Crystal structure determinations

Data were collected on a Stoe IPDS diffractometer; Stoe IPDS software [16] and SHELXL97 [17] were used for the data reduction, solution and refinement. ORTEP figures were drawn with the programme Ortep-3 for Windows [18]. The programme Mercury v. 2.4 [19,20] was used for packing analysis.

2.5. $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$

$C_{126}H_{152}Cl_4N_8O_{46}Zn_{12}$, $M = 3440.83$, yellow block, monoclinic, space group *C2/c*, $a = 21.781(4)$, $b = 19.2022(19)$, $c = 20.160(3)$ Å, $\beta = 112.542(12)°$, $U = 7787.5(21)$ Å^3, $Z = 2$, $D_c = 1.460$ Mg m^{-3}, μ(Mo Kα) = 1.957 mm^{-1}, $T = 173$ K. Total 48229 reflections, 6875 unique, $R_{int} = 0.0715$. Refinement of 5849 reflections (516 parameters) with $I > 2\sigma(I)$ converged at final $R1 = 0.0586$ ($R1$ all data = 0.0679), $wR2 = 0.1606$ ($wR2$ all data = 0.1695), GOF = 1.053.

2.6. $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$

$C_{158}H_{168}N_{10}O_{41}Zn_{10}$, $M = 3516.94$, orange block, triclinic, space group $P\bar{1}$, $a = 13.820(3)$, $b = 17.223(3)$, $c = 17.829(3)$ Å, $\alpha = 88.671(15)$, $\beta = 73.776(14)$, $\gamma = 78.904(14)°$, $U = 3996.5(12)$ Å^3, $Z = 1$, $D_c = 1.460$ Mg m^{-3}, μ(Mo Kα) = 1.553 mm^{-1}, $T = 173$ K. Total 51236 reflections, 15690 unique, $R_{int} = 0.0805$. Refinement of 11934 reflections (1090 parameters) with $I > 2\sigma(I)$ converged at final $R1 = 0.0615$ ($R1$ all data = 0.0833), $wR2 = 0.1581$ ($wR2$ all data = 0.1718), GOF = 1.053.

3. Results and discussion

3.1. Ligand $H_2$1

To the best of our knowledge, the detailed characterization of H_2**1** has not previously been described, despite its use in complexation studies [14,15]. The ligand was isolated as an orange solid from the condensation of 2-aminophenol with 3-ethoxy-2-hydroxybenzaldehyde. The orange colour arises from a broad band ($\lambda_{max} = 350$ nm) in the electronic absorption spectrum that extends into the visible region (Fig. 1). The base peak in the ESI mass spectrum appeared at *m/z* 280.0 and was assigned to $[M+Na]^+$.

The ^1H and ^{13}C NMR spectra of H_2**1** in acetone-d_6 were consistent with the structure shown in Scheme 1, and were assigned using 2D techniques. Observation of cross peaks in the NOESY spectrum between pairs of signals for protons $H^{N=CH}/H^{A5}$ and $H^{N=CH}/H^{B3}$ followed by use of the COSY spectrum, allowed the signals for the aromatic rings to be assigned. The NOESY spectrum revealed cross peaks between H^{B6} and both OH proton signals. This is understood by the additional observation of chemical exchange (EXSY) peaks between signals assigned to the two OH protons (δ 13.33 and 8.52 ppm) and residual H_2O (δ 2.86 ppm) in the acetone-d_6 (Fig. 2), and the exchange process makes it difficult to unambiguously assign the individual OH resonances.

3.2. Reaction of $H_2$1 with zinc(II) chloride

The reaction of H_2**1** with anhydrous $ZnCl_2$ (1:2 equivalents) in a mixture of CH_2Cl_2 and MeOH in the presence of base (LiOH) resulted in the precipitation of a yellow solid that analysed as $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$. The ESI mass spectrum exhibited four pairs of peak envelopes at *m/z* 643.2 and 665.2, 962.4 and 984.4, 1283.4 and 1305.4, 1602.3 and 1624.3, the lowest mass peak being the base peak. The *m/z* values and isotope distributions were consistent with pairs of ions $[Zn_n\mathbf{1}_n+H]^+$ and $[Zn_n\mathbf{1}_n+Na]^+$ for $n = 2, 3, 4$ and 5.

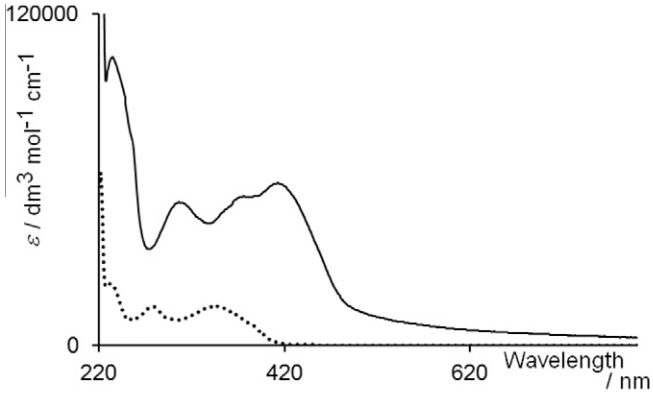

Fig. 1. Solution (CH_2Cl_2) electronic absorption spectra of H_2**1** (····), and $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ (—).

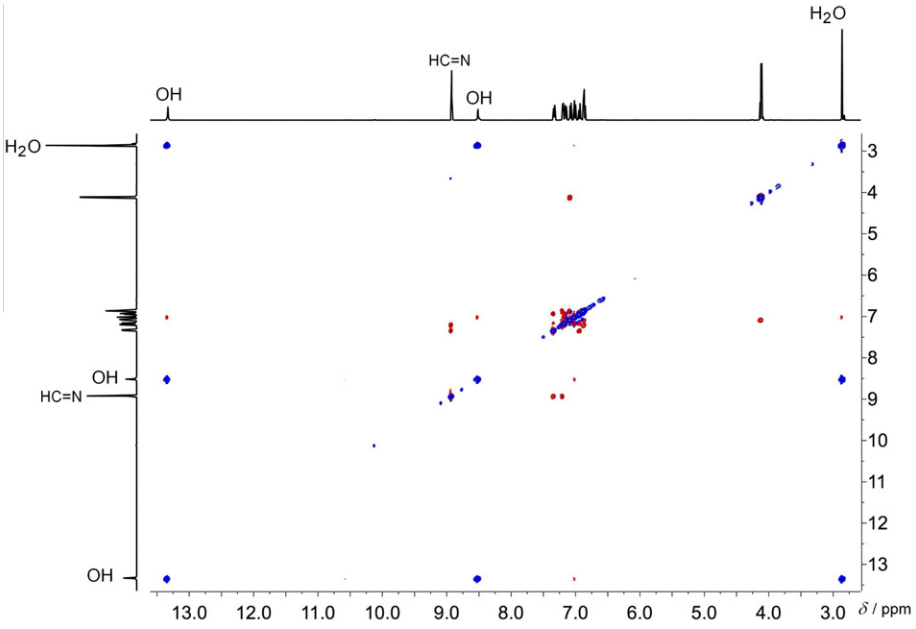

Fig. 2. 500 MHz NOESY spectrum of H_2**1** in acetone-d_6 showing EXSY cross peaks arising from OH/H_2O exchange, in addition to NOESY cross peaks.

The electronic absorption spectrum of a CH_2Cl_2 solution of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ is shown in Fig. 1, and the relative values of extinction coefficients for free ligand H_2**1** and the complex are consistent with the presence of multinuclear species in solution. The compound $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ is emissive both in CH_2Cl_2 solution and in the solid state. Upon excitation at 365 nm, solutions exhibit a broad emission centred at 509 nm. The solid bulk sample was layered onto the surface of a quartz plate, and for this sample, λ_{em} was observed at 527 nm (λ_{ex} = 400 nm). Solution ^1H NMR spectroscopic data for the complex are discussed after the structural characterization.

Evaporation of a CH_2Cl_2/MeOH solution of the bulk sample $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ over a period of a month at ambient temperature yielded yellow blocks. Slow evaporation of the mother liquor over several weeks gave a few orange blocks in addition to further yellow blocks. The orange crystals were separated manually. For both compounds, single crystals of X-ray quality could be selected. The major (yellow) and minor (orange) components were found to be $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$ and $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$, respectively.

The compound $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$ crystallizes in the monoclinic space group *C2/c* with half of one $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]$ cluster in the asymmetric unit. The second half is generated by a C_2 axis and the complete cluster is depicted in Fig. 3. The figure shows two, symmetry-related metal-bound MeOH molecules (atoms O8 and C80). However, while atom O8 is full occupancy, atom C80 is half-occupancy, and the coordinated ligand has been modelled as a half-occupancy MeOH and half-occupancy H_2O. The overall stoichiometry of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]$ is different from the best fit to the elemental analytical data, i.e. $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$, and we assume that partial MeOH-for-H_2O ligand exchange occurs during

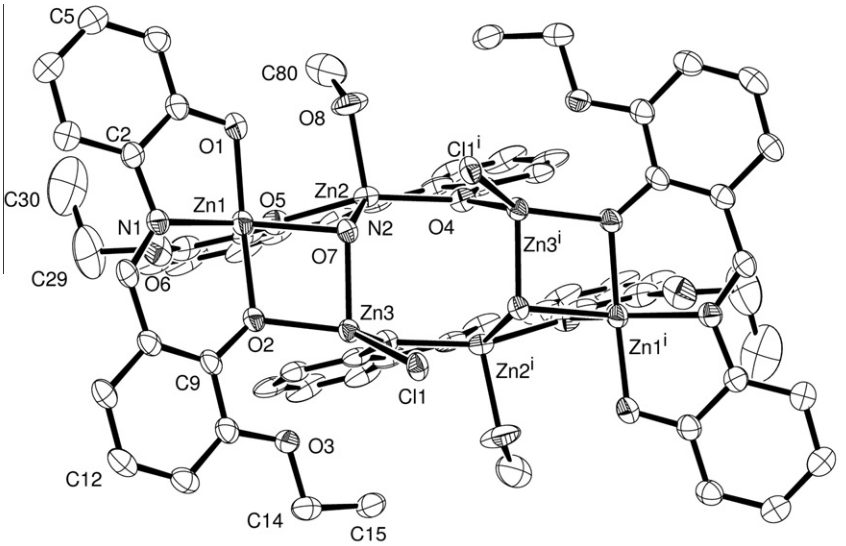

Fig. 3. Structure of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]$ in $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$ (ellipsoids plotted at 20% probability for clarity; H atoms omitted). Atom C80 is 50% occupancy; atom O8 is modelled as being common to a coordinated MeOH and a coordinated H_2O molecule. Symmetry code i = $1 - x, y, {}^1/_2 - z$.

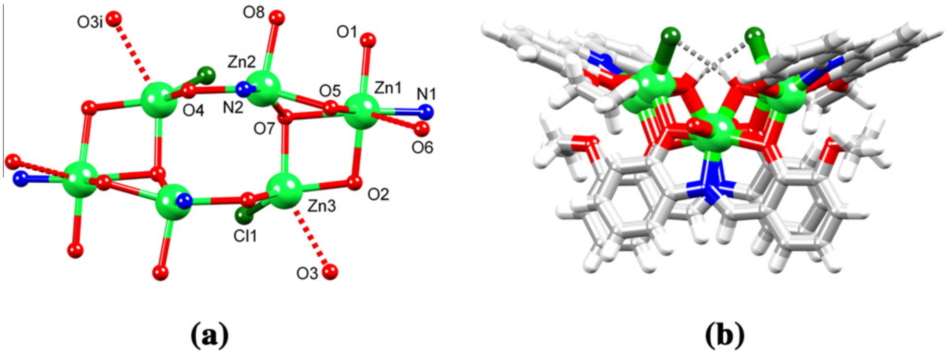

Fig. 4. (a) The $\mathrm{Zn_6Cl_2N_4O_{16}}$-core of $[\mathrm{Zn_6}(\mathbf{1})_4\mathrm{Cl_2(OH)_2(OH_2)(MeOH)}]$ in $2\{[\mathrm{Zn_6}(\mathbf{1})_4\mathrm{Cl_2(OH)_2(OH_2)(MeOH)}]\}\cdot 4\mathrm{MeOH}\cdot 8\mathrm{H_2O}$. The labelling scheme is as in Fig. 3. Bond distances: Zn1–O1 = 2.000(3), Zn1–O2 = 2.038(2), Zn1–N1 = 2.048(3), Zn1–O5 = 2.013(3), Zn1–O7 = 2.164(2), Zn2–O4 = 2.071(3), Zn2–O5 = 2.043(3), Zn2–O7 = 1.973(2), Zn2–O8 = 2.013(3), Zn2–N2 = 2.030(3), Zn3–O4^{i} = 1.955(2), Zn3–O2 = 1.961(3), Zn3–O7 = 2.048(2), Zn3–Cl1 = 2.2317(9) Å. (b) A view through the $[\mathrm{Zn_6}(\mathbf{1})_4\mathrm{Cl_2(OH)_2(OH_2)(MeOH)}]$ molecule looking down the a-axis.

crystallization from the MeOH/$\mathrm{CH_2Cl_2}$ solution. The structure of $[\mathrm{Zn_6}(\mathbf{1})_4\mathrm{Cl_2(OH)_2(OH_2)(MeOH)}]$ is best described in terms of a $\{\mathrm{Zn_6}(\mu\text{-O})_6(\mu_3\text{-O})_2\}$ core (Fig. 4). Each of the μ-O bridges originates from a phenoxy group of ligand **1** (O2 from one independent ligand, and O4 and O5 from the other), while the μ_3-O donor is supplied by a hydroxido ligand. The fourth phenoxy group (O1) occupies a terminal site in the coordination sphere of Zn1, and the two ethoxy O atoms (O3 and O6) are involved in weak contacts to Zn3 (Zn3–O3 = 2.589(2) Å) and Zn1 (Zn1–O6 = 2.601(4) Å), respectively (Fig. 4). The imino N atoms of the two independent ligands bind to Zn1 and Zn2, while Zn3 is coordinated by a chlorido ligand. Taking into account the weak contacts to O3 and O6, atoms Zn1, Zn2 and Zn3 are 6-, 5- and 5-coordinate, respectively. A search of the Cambridge Structural Database (v. 5.33 with February 2012 updates) using Conquest [19] for the cyclic $\{\mathrm{Zn_6}(\mu\text{-O})_6\}$ motif present in this compound gave 41 occurrences for discrete molecular systems, while adding the restriction of the two μ_3-O caps in the positions shown in Fig. 4 reduced this to only one match [21]. The $\{\mathrm{Zn_6}(\mu\text{-O})_6(\mu_3\text{-O})_2\}$ unit is folded so that the two μ_3-hydroxido ligands form hydrogen bonds to the chlorido ligands (O7H7…Cl1^{i} = 2.38(2), O7…Cl1^{i} = 3.155(2) Å, O7–H7…Cl1^{i} = 154(2)°, Fig. 4b). Two symmetry related $[\mathbf{1}]^{2-}$ ligands lie over one another and engage in π-stacking of the aromatic rings containing atom C16 and C24^{i} (Fig. 4b, angle between the least squares planes of the rings = 6.7°, and centroid…centroid distance = 3.82 Å). The solvent molecules are disordered and have been modelled as partial occupancy MeOH and $\mathrm{H_2O}$ molecules; the extent of disorder makes discussion of any intermolecular contacts meaningless.

The arrangement of the ligands leads to two imine environments, and this can be used to assess the retention of the cluster in solution. The bulk sample was poorly soluble in $\mathrm{CDCl_3}$ but a sufficiently well resolved 400 MHz ^{1}H NMR spectrum could be obtained. The spectrum indicated the presence of at least four species in solution, and the aromatic region between δ 7.60 and 6.40 ppm exhibited overlapping signals. More informative was a set of four singlets at δ 8.91, 8.90, 8.89 and 8.88 ppm, accompanied by a set of overlapping singlets at δ 8.175, 8.17, 8.15 and 8.145 ppm (Fig. 5). We assign these signals to the $\mathrm{H_{imine}}$ protons. The total relative integrals of the $\mathrm{H_{imine}}$:$\mathrm{H_{aromatic}}$ was 1:7, consistent with that expected for ligand $[\mathbf{1}]^{2-}$. Evidence for multiple solution species also comes from the electrospray mass spectrum of a methanol solution of the bulk sample. Peak envelopes are observed at *m/z* 643.2, 665.2, 962.4, 984.4, 1283.4, 1305.4, 1602.3 and 1624.3 and the isotope distributions are consistent with assignemts to the ions $[\mathrm{Zn_2}\mathbf{1}_2\mathrm{+H}]^{+}$, $[\mathrm{Zn_2}\mathbf{1}_2\mathrm{+Na}]^{+}$, $[\mathrm{Zn_3}\mathbf{1}_3\mathrm{+H}]^{+}$, $[\mathrm{Zn_3}\mathbf{1}_3\mathrm{+Na}]^{+}$, $[\mathrm{Zn_4}\mathbf{1}_4\mathrm{+H}]^{+}$, $[\mathrm{Zn_4}\mathbf{1}_4\mathrm{+Na}]^{+}$, $[\mathrm{Zn_5}\mathbf{1}_5\mathrm{+H}]^{+}$ and $[\mathrm{Zn_5}\mathbf{1}_5\mathrm{+Na}]^{+}$, respectively.

Single crystal structure determination of the minor, orange component (see above) revealed this to be $2\{[\mathrm{Zn_5}(\mathbf{1})_5\mathrm{(MeOH)(OH_2)}]\}\cdot 6\mathrm{MeOH}\cdot\mathrm{H_2O}$. The pentanuclear cluster is shown in Fig. 6. The compound crystallizes in the triclinic space group $P\bar{1}$, and each Zn atom is independent. Atoms Zn1, Zn3 and Zn4 are octahedrally sited with an O_5N-coordination sphere. The range of Zn–O bond distances for Zn1 is 1.977(2)–2.386(2) Å, for Zn3 is 2.015(2)–2.443(2) Å and for Zn4 is 1.989(2)–2.352(2) Å; Zn–N bond lengths are 2.034(3) Å for Zn1, 2.045(3) Å for Zn3, and 2.023(3) Å for Zn4. Atoms Zn2 and Zn5 are 5-coordinate. Whereas the geometry around Zn5 is square-based pyramidal (τ = 0.02 [22]), that around Zn2 is in between square-based pyramidal and trigonal bipyramidal (τ = 0.45). The Zn–O bond lengths lie in the range 1.957(2)–2.137(2) Å for Zn2 and 1.969(2)–2.080(2) Å for Zn5, and the Zn–N distances are 2.047(3) and 2.058(3) Å for Zn2 and Zn5, respectively. Two of the ethoxy groups are involved in coordination (atoms O9 and O15) while the remaining three face away from the cluster unit. The $\mathrm{Zn_5N_5O_{14}}$-unit of $[\mathrm{Zn_5}(\mathbf{1})_5\mathrm{(MeOH)(OH_2)}]$ is shown in Fig. 7 and consists of a $\{\mathrm{Zn_5}(\mu\text{-O})_3(\mu_3\text{-O})_3\}$-core. Each bridging oxygen atom in this unit originates from a phenoxy unit in a ligand. A search of the CSD (v. 5.33 with February

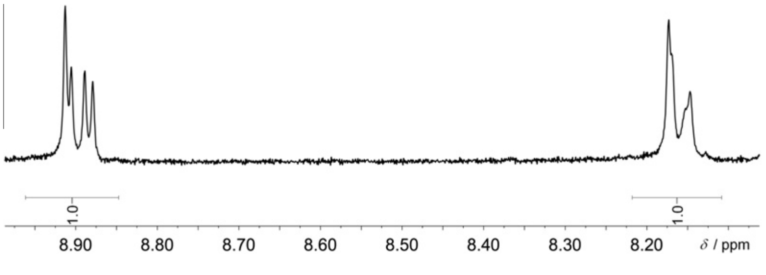

Fig. 5. Signals arising from imine protons in the 400 MHz spectrum of dissolved bulk sample of $[\mathrm{Zn_6}(\mathbf{1})_4\mathrm{Cl_2(OH)_2(OH_2)_2}]$ in $\mathrm{CDCl_3}$.

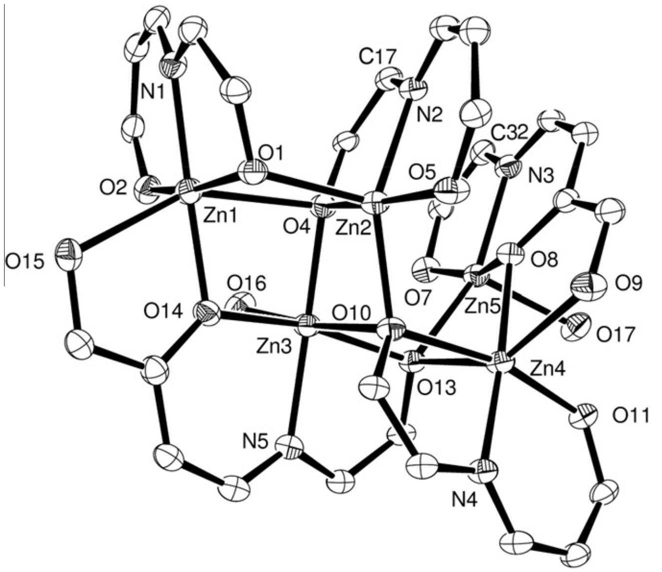

Fig. 6. The cluster unit in $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$ (ellipsoids plotted at 20% probability for clarity). For clarity, H atoms are omitted, as are C atoms of phenyl and ethyl groups. Atoms O16 and O17 belong to H_2O and MeOH ligands, respectively.

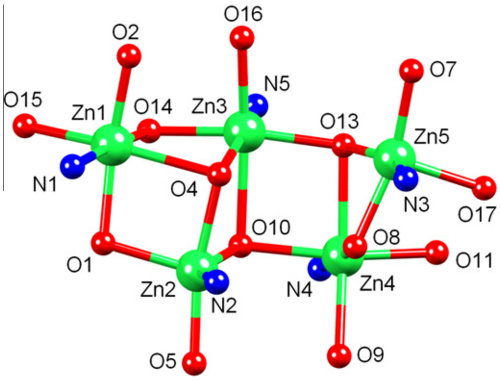

Fig. 7. The $Zn_5N_5O_{14}$-core of $[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]$ in $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$. The labelling scheme is as in Fig. 6.

2012 updates) [19] for the $\{Zn_5(\mu\text{-}O)_3(\mu_3\text{-}O)_3\}$-cluster shown at the centre of Fig. 7 reveals that this is the first report of this unit in a discrete molecule, although the motif appears within larger clusters [21,23–25].

As in $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]$, face-to-face π-stacking of aromatic rings contributes to the stabilization of the structure of the $[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]$ cluster. However, these interactions are only weak, the most favourable interaction being achieved between the phenyl rings containing atoms C32 and C17 (angle between the least squares planes = 3.3° and distance between ring centroids = 4.4 Å). This inter-centroid separation is at the upper limit of that considered by Janiak [26] in an assessment of π-stacking on pyridine rings in metal complexes. The H atoms of the coordinated H_2O ligand (atom O16) were located in the difference map. One is involved in an intramolecular hydrogen-bond to the phenoxy unit containing O2 (O16H161…O2 = 2.01(2), O16…O2 = 2.774(4) Å, O16–H161…O2 = 149(3)°). The second forms a hydrogen bond to the MeOH solvent molecule containing atom O200 (O16H160…O200 = 1.768(18), O16…O200 = 2.499(8) Å, O16–H160…O200 = 140.0(13)°). Remaining solvent molecules are disordered and have been modelled as partial occupancy H_2O or MeOH.

The very small number of crystals of $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$ that were obtained prevented characterization of the bulk sample. Nevertheless, isolation of this compound supports the conclusions drawn from solution data for the bulk sample of the hexanuclear compound, namely that dissolution of the bulk material results in the formation of a number of species of varying nuclearity.

4. Conclusions

Multinuclear zinc(II)-containing clusters are assembled using the *O,O′,N,O″*-donor set of the conjugate base of the simple Schiff base ligand $H_2\mathbf{1}$. The electrospray mass spectrum of a MeOH solution of a bulk sample of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ shows the presence of species ranging in nuclearity from two to five, while the ^{1}H NMR spectrum of a $CDCl_3$ solution of the bulk sample confirms the presence of at least four species. Crystals of $2\{[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)(MeOH)]\}\cdot 4MeOH\cdot 8H_2O$ and $2\{[Zn_5(\mathbf{1})_5(MeOH)(OH_2)]\}\cdot 6MeOH\cdot H_2O$ were grown from the same solution of $[Zn_6(\mathbf{1})_4Cl_2(OH)_2(OH_2)_2]$ in CH_2Cl_2/MeOH, and structural determinations confirm clusters with $\{Zn_6(\mu\text{-}O)_6(\mu_3\text{-}O)_2\}$- and $\{Zn_5(\mu\text{-}O)_3(\mu_3\text{-}O)_3\}$-cores, respectively.

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Appendix A. Supplementary data

CCDC 880551 and 880552 contains the supplementary crystallographic data for this paper;. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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