Polynuclear Zinc(II) Complexes of Phenol–Imine and –Amine Macrocycles†

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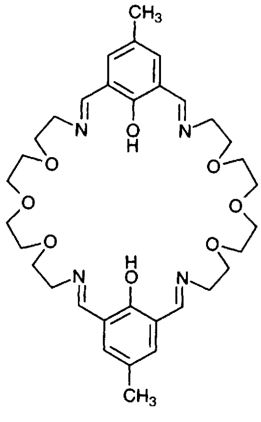
The template condensation of 2,6-diformyl-4-methylphenol with 1,11-diamino-3,6,9-trioxaundecane using zinc(II) acetate as the metal source, followed by addition of an excess of $NaClO_4$, gave a tetranuclear zinc(II) complex $[Zn_4L^1(\mu\text{-}O_2CMe)_4][ClO_4]_2$ **1**, where H_2L^1 is a [2 + 2] tetra-Schiff-base macrocycle. A single-crystal X-ray analysis of the dichloromethane adduct, **1**·$2CH_2Cl_2$, revealed that this complex cation is centrosymmetric and contains two pairs of zinc ions bridged by a phenolic oxygen and two acetate ligands. Recrystallisation of this complex from a hydrous methanolic solution gave another tetranuclear complex, $[Zn_4L^1(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)_2][ClO_4]_2\cdot 2H_2O$ **2**, which was also structurally characterised. While the four zinc ions are encapsulated in the macrocycle as observed for **1**, in complex **2** the two dimeric units formed by phenoxo- and acetato-bridges are further connected by two hydroxo bridges. Proton NMR spectroscopy has shown that this structural conversion is reversible and depends on the presence of water or acetic acid in solution. Treatment of complex **1** (or **2**) with $NaBH_4$ in methanol gave a dinuclear zinc complex, $[Zn_2L^2][ClO_4]_2\cdot H_2O$ **3**, together with a metal-free phenol–amine macrocycle, H_2L^2, which is a reduced form of H_2L^1. Both complex **3** and H_2L^2, have been characterised on the basis of spectroscopic data.

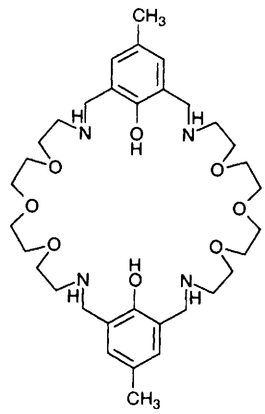
Syntheses of polynuclear transition-metal complexes have been the subject of much attention in co-ordination chemistry owing to the recognition of the role played by polynuclear structures in metalloproteins.[1] In particular, tetranuclear metal complexes in which the metal ions are located in close proximity are of current interest,[2,3] as models of multi-electron redox reactions, such as the oxygen-evolving complex (OEC) of photosystem II in green plants.[4]

In order to organize four metal ions in a predetermined arrangement, the use of specially designed tetranucleating macrocyclic ligands is in principle the most direct and effective way. In fact, this synthetic strategy has been successful to some extent for certain metal ions, *e.g.* for Zn^{II},[2a,b] Ni^{II} [2a,c] and Cu^{II},[2d] whilst it has been unsuccessful so far for manganese.[5] Another preparative route to attain such tetranuclear structures, which has been most widely used, is the utilisation of the self-aggregation properties of dinuclear species.[3] Several phenoxo-bridged dinuclear complexes often self-aggregate to form tetranuclear complexes with the help of exogenous bridging ligands such as oxo and hydroxo,[3a] oxo and bromo,[3b] and oxo and carboxylato,[3b,c] *etc.* A recently reported tetranuclear copper(II) complex[6] was also such an assembly type, and was the first example of a crystallographically determined $\mu_4\text{-}O_2{}^{2-}$ co-ordination mode in a copper(II) complex. This peroxo co-ordination mode is very fascinating with respect to dioxygen release catalysed by the tetranuclear Mn cluster of OEC in photosystem II, in which $\mu_4\text{-}O_2{}^{2-}$ co-ordination has been under discussion[7] as an intermediate in the oxidation of water.[3]

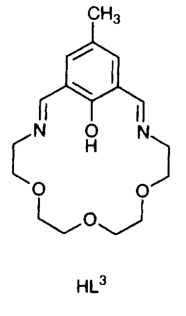
Our approach to new tetranuclear complexes has been based on the synthesis of large macrocycles which contain two phenoxo-bridged dinuclear cores possessing an intramolecular self-assembling property. Tetranuclear structures derived from such macrocycles are expected to be thermodynamically stabilised by the macrocyclic effect[8] and, thus, their reactivities can easily be investigated in solution. Here we report such a macrocyclic ligand, H_2L^1, which has been obtained by the template condensation of 2,6-diformyl-4-methylphenol and



H_2L^1



H_2L^2



HL^3

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

1,11-diamino-3,6,9-trioxaundecane using zinc(II) acetate as the template core. The structures of $[Zn_4L^1(\mu-O_2CMe)_4][ClO_4]_2\cdot 2CH_2Cl_2$ (**1**: pre-aggregated form) and $[Zn_4L^1(\mu-OH)_2(\mu-O_2CMe)_2][ClO_4]_2$ (**2**: aggregated form) in both the solid state and solution have been characterised, by X-ray crystallography and NMR spectroscopy, respectively. Further, the chemistry of the other macrocycles H_2L^2 and HL^3 is also briefly discussed; the former ligand has been obtained by reducing H_2L^1 whereas the latter has been obtained by the metal-free Schiff-base condensation of the same diamine and dialdehyde.

Experimental

Materials.—2,6-Diformyl-4-methylphenol[9] and 1,11-diamino-3,6,9-trioxaundecane[10] were respectively synthesised by a slight modification of the literature methods. Solvents used for syntheses were distilled prior to use. Deuteriated solvents $CDCl_3$ (99.8%, Merck), D_2O (99.8%, Merck), CD_3CN (99.8%, Nippon Sanso) and CD_3OD (99.8%, Nakalai tesque) were commercially obtained and used for NMR measurements without further purification. All other chemicals were of reagent grade and used as received.

Preparations.—$[Zn_4L^1(\mu-O_2CMe)_4][ClO_4]_2$ **1**. The compounds 2,6-diformyl-4-methylphenol (5.00 g, 0.031 mol) and $Zn(O_2CMe)_2$ (11.18 g, 0.062 mol) were dissolved together in methanol (150 cm^3) under reflux. To the resultant solution 1,11-diamino-3,6,9-trioxaundecane (5.86 g, 0.031 mol) in methanol (30 cm^3) was added dropwise. The yellow reaction mixture was heated under reflux for 30 min and then an excess of $NaClO_4$ (30.4 g, 0.248 mol) added. Upon standing at room temperature a yellow crystalline precipitate started to separate. After 2 h the precipitate was collected, washed with methanol, diethyl ether, and then air-dried. Yield: 18.0 g.

The precipitate is invariably contaminated with a small amount of $[Zn_4L^1(\mu-OH)_2(\mu-O_2CMe)_2][ClO_4]_2\cdot 2H_2O$ **2**. The extent of contamination depends on the amount of water in the solvent used (see below). Recrystallisation from a mixture of dry methanol and dry dichloromethane gave yellow needle-like crystals, which very easily lost lattice solvent (CH_2Cl_2) in air to become a powder. The yellow powder had a composition consistent with the chemical formula $[Zn_4L^1(\mu-O_2CMe)_4][ClO_4]_2$ (Found: C, 37.70; H, 4.30; N, 4.15; Zn, 19.55. Calc. for $C_{42}H_{58}Cl_2N_4O_{24}Zn_4$: C, 37.80; H, 4.40; N, 4.20; Zn, 19.60%). NMR (CD_3CN): ^1H, δ 8.43 (s, 4 H, imine H), 7.42 (s, 4 H, aryl), 3.80–3.89 [m, 24 H, $CH_2(CH_2OCH_2)_3CH_2$], 3.67 [t, 8 H, $CH_2(CH_2OCH_2)_3CH_2$], 2.25 (s, 6 H, aryl Me), 1.96 (s, 12 H, $MeCO_2$); ^{13}C, δ 181.13, 173.49, 165.35, 144.22, 127.63, 121.13, 72.99, 70.35, 69.90, 58.36, 23.54, 19.46.

$[Zn_4L^1(\mu-OH)_2(\mu-O_2CMe)_2][ClO_4]_2\cdot 2H_2O$ **2**. This complex was prepared by the same method as that for **1**, using a mixture of methanol and water (10:1) as solvent. Yield: 90%. The yellow crystalline product was further recrystallised from the same mixed solvent to give yellow needles, which were very stable in air (Found: C, 35.20; H, 4.55; N, 4.25; Zn, 20.60. Calc. for $C_{38}H_{58}Cl_2N_4O_{24}Zn_4$: C, 35.45; H, 4.35; N, 4.25; Zn, 20.30%). NMR (CD_3CN): ^1H, δ 8.12 (s, 4 H, imine H), 7.02 (s, 4 H, aryl), 4.16 (s, 2 H, OH), 3.63–4.02 [m, 32 H, $CH_2(CH_2OCH_2)_3CH_2$], 2.19 (s, 6 H, aryl Me), 1.96 (s, 6 H, $MeCO_2$); ^{13}C, δ 181.99, 173.53, 165.76, 144.83, 126.84, 120.73, 70.85, 68.98, 68.07, 59.46, 23.77, 19.55.

$[Zn_2L^2][ClO_4]_2\cdot H_2O$ **3** *and isolation of metal-free* H_2L^2. To a suspension of complex **2** (25.0 g, 0.019 mol) in methanol (400 cm^3) was added dropwise an aqueous solution (25 cm^3) of $NaBH_4$ (7.35 g, 0.194 mol) over a period of 30 min. After 2 h of vigorous stirring, water (500 cm^3) was added. The resultant off-white precipitate was collected, washed successively with water, methanol and diethyl ether and dried in air. Yield: 17.57 g (93%). Recrystallisation of the product from hot acetonitrile gave white needles (Found: C, 41.35; H, 5.45; N, 5.40; Zn, 13.15. Calc. for $C_{34}H_{56}Cl_2N_4O_{17}Zn_2$: C, 41.05; H, 5.70; N, 5.65; Zn, 13.30%). NMR (CD_3CN): ^1H, δ 6.88 (s, 4 H, aryl), 4.36 (t, 4 H, NH), 3.86–4.04 (m, 8 H, aryl CH_2N), 2.76–3.27 [m, 32 H, $CH_2(CH_2OCH_2)_3CH_2$], 2.22 (s, 6 H, aryl Me); ^{13}C, δ 159.64, 132.02, 126.30, 125.15, 67.80, 64.94, 58.94, 51.10, 47.42, 20.25.

Standard[11] demetallation of complex **3**, using H_4edta (ethylenediaminetetraacetic acid) chelator and extracting with dichloromethane, quantitatively gave the metal-free macrocycle H_2L^2 as a pale yellow oil. Yield: 98%. Mass spectrum (positive-ion FAB): *m/z* 649 (M^+). ^1H NMR ($CDCl_3$): δ 6.80 (s, 4 H, aryl), 5.61 (br, 6 H, NH and OH), 3.82 (s, 8 H, aryl CH_2N), 3.62 [m, 24 H, $CH_2(CH_2OCH_2)_3CH_2$], 2.81 [t, 8 H, $CH_2(CH_2OCH_2)_3CH_2$], 2.10 (s, 6 H, aryl Me).

This macrocycle was also obtained in high yield (>90%) from complex **1** using a series of reduction and demetallation procedures.

$[HL^3][HPF_6]$. An equimolar mixture of 2,6-diformyl-4-methylphenol (0.352 g, 0.002 mol) and 1,11-diamino-3,6,9-trioxaundecane (0.412 g, 0.002 mol) in methanol (200 cm^3) gave a clear yellow solution. Addition of NH_4PF_6 (0.342 g, 0.002 mol) immediately yielded a yellow precipitate. This product was recrystallised from acetonitrile to give a [1 + 1] Schiff-base condensation product as the hydrogen hexafluorophosphate salt in a cubic crystalline form. Yield: 0.24 g (25%). Mass spectrum (positive-ion FAB): *m/z* 321 $[(HL^3)^+]$ (Found: C, 43.80; H, 5.45; N, 6.00. Calc. for $C_{17}H_{25}Cl_2N_2O_4PF_6$: C, 43.80; H, 5.40; N, 6.00%). ^1H NMR (CD_3CN): δ 14.45 (br, 2 H, H^+ and aryl OH), 8.43 and 8.38 (s, 2 H, imine H), 7.58 (s, 2 H, aryl), 3.88 [q, 4 H, $CH_2(CH_2OCH_2)_3CH_2$], 3.56–3.68 [m, 12 H, $CH_2(CH_2OCH_2)_3CH_2$], 2.24 (s, 3 H, aryl Me).

Instruments, Analyses and Measurements.—The C, H, N analyses were carried out at the Inorganic Chemistry Laboratory, Shimane University, Japan. Zinc analyses were made on a Shimadzu AA-680 atomic absorption–flame emission spectrophotometer. Infrared spectra were recorded on a JASCO FT/IR-300 spectrophotometer using KBr discs. Molar conductances were measured in acetonitrile (10^{-3} mol dm^{-3}) on a TOA Electronics CM-50AT conductivity meter at 25 °C. Proton and ^{13}C NMR spectra were recorded using a JEOL EX-270 spectrometer, chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Fast atom bombardment (FAB) mass spectra were measured using a mixture of dithiothreitol and dithioerythritol (3:1) as matrix on a TSQ-70 mass spectrometer (Finningen MAT Corporation).

Crystal-structure Determination.—The yellow needle-like crystals of $\mathbf{1}\cdot 2CH_2Cl_2$ readily lost CH_2Cl_2 in air to become a powder. Therefore, the single crystal which was prepared by recrystallisation from a solvent mixture of dry MeOH and CH_2Cl_2 was picked directly from the mother-liquor, coated with hydrocarbon grease, sealed with the mother-liquor in a capillary tube, and used for X-ray crystallography. In contrast, the yellow needle-like crystals of **2** are so stable in air that the single crystal was mounted in a capillary without coating or sealing with the mother-liquor.

Crystal data and details pertaining to the data collection are given in Table 1. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 Express diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) in the ω–2θ scan mode. The data were corrected for crystal decomposition, Lorentz and polarisation effects, and absorption from the empirical ψ-scan data. Accurate unit-cell parameters were obtained by a least-squares fit of 25 reflections with $20° \leqslant 2\theta \leqslant 30°$. The structures were solved by direct methods and refined using full-matrix least-squares procedures. For $\mathbf{1}\cdot 2CH_2Cl_2$, all the non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. All the hydrogen atoms were placed in calculated positions and included in the final refinement as fixed scatters (d_{C-H} 0.95 Å, B_{eq} 5.00 $Å^2$). For **2**, all the non-hydrogen atoms from L^{2-} and the acetate groups were readily located and refined with anisotropic

Table 1 Crystallographic data and details of the structure determinations for complexes **1**·2CH_2Cl_2 and **2**

	1·2CH_2Cl_2	**2**
Formula	$C_{44}H_{62}Cl_6N_4O_{24}Zn_4$	$C_{38}H_{58}Cl_2N_4O_{24}Zn_4$
M	1505.3	1287.4
Crystal system	Monoclinic	Monoclinic
Colour, habit	Yellow, needle	Yellow, needle
Space group	$P2_1/c$	$P2_1/a$
a/Å	8.625(3)	13.891(1)
b/Å	12.232(2)	31.215(3)
c/Å	28.816(5)	14.076(1)
β/°	92.028(25)	118.909(8)
U/Å^3	3038(1)	5343(1)
Z	2	4
D_c/g cm^{-3}	1.65	1.60
D_m/g cm^{-3}	—	1.61
T/°C	20 ± 1	20 ± 1
F(000)	1320	2 640
μ/cm^{-1}	17.615	19.982
Radiation (λ/Å)[a]	0.710 73	0.710 73
Transmission factor	0.999–0.781	1.00–0.975
Crystal size/mm	0.50 × 0.25 × 0.10	0.50 × 0.20 × 0.08
2θ range/°	5.32–54.16	4.96–52.94
Octants collected	$0 \leqslant h \leqslant 11, 0 \leqslant k \leqslant 15, -36 \leqslant l \leqslant 36$	$0 \leqslant h \leqslant 17, 0 \leqslant k \leqslant 39, -17 \leqslant l \leqslant 17$
Total reflections	6644	11 008
Unique reflections [$I > 3\sigma(I)$]	2779	3822
No. of variables	370	541
R,[b] R'[c]	0.0383, 0.0445	0.0861, 0.1213
Maximum residual electron density/e Å^{-3}	0.364	1.298

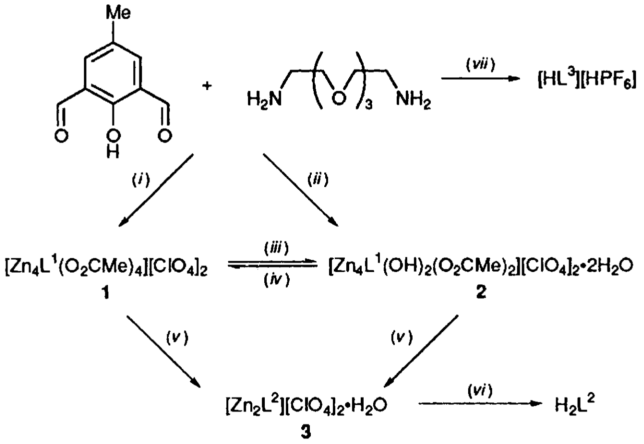
[a] Mo-Kα from graphite monochromator. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F) + 0.0004F^2$.

Table 2 Selected interatomic distances (Å) for complexes **1**·2CH_2Cl_2 and **2** with estimated standard deviations (e.s.d.s) in parentheses

1·2CH_2Cl_2			
Zn(1)–O(1)	2.039(3)	Zn(2)–O(6)	1.945(4)
Zn(1)–O(2)	2.315(3)	Zn(2)–O(8)	1.949(4)
Zn(1)–O(5)	1.951(3)	Zn(2)–N(2)	1.993(4)
Zn(1)–O(7)	1.953(4)	Zn(1) ··· Zn(2)	3.1588(9)
Zn(1)–N(1)	1.991(4)	Zn(1) ··· Zn(1′)	8.0773(8)
Zn(2)–O(1)	2.044(3)	Zn(1) ··· Zn(2′)	7.6248(9)
Zn(2)–O(4)	2.336(3)	Zn(2) ··· Zn(2′)	8.4255(9)
2			
Zn(1)–O(1)	2.043(9)	Zn(3)–O(4)	2.366(12)
Zn(1)–O(2)	2.342(11)	Zn(3)–O(5)	2.028(10)
Zn(1)–O(10)	1.921(11)	Zn(3)–O(10)	1.916(11)
Zn(1)–O(11)	2.001(13)	Zn(3)–O(13)	1.957(11)
Zn(1)–N(1)	1.996(13)	Zn(3)–N(3)	2.05(2)
Zn(2)–O(1)	2.052(9)	Zn(4)–O(5)	2.033(9)
Zn(2)–O(8)	2.506(9)	Zn(4)–O(6)	2.510(9)
Zn(2)–O(9)	1.938(10)	Zn(4)–O(9)	1.895(10)
Zn(2)–O(12)	1.956(10)	Zn(4)–O(14)	1.955(12)
Zn(2)–N(2)	1.971(13)	Zn(4)–N(4)	2.027(13)
Zn(1) ··· Zn(2)	3.233(2)	Zn(2) ··· Zn(3)	4.784(3)
Zn(1) ··· Zn(3)	3.407(3)	Zn(2) ··· Zn(4)	3.414(3)
Zn(1) ··· Zn(4)	4.517(2)	Zn(3) ··· Zn(4)	3.221(2)

Symmetry code ′: $-x, -y, 1 - z$.

thermal parameters. Since the successive refinements and Fourier-difference syntheses gave many peaks around the two perchlorate ions, the ions were treated as disordered and fixed with isotropic thermal parameters at the final stage of the refinement; the 16 oxygen atoms were treated with the same occupancy factor of 0.50. Although two water molecules per asymmetric unit were predicted from the elemental analysis, all attempts to locate them were in vain, because of diverging temperature factors. Therefore, no water molecule was included in the final stage. No effort was made to find and calculate the positions of the hydrogen atoms. All computations were performed on a VAX station computer (4000-VLC) using the Enraf-Nonius MolEN programs.[12] Crystallographic diagrams were drawn using the ORTEP program[13] for **1** and the Chem3D software[14] for **2**. Selected bond distances for complexes **1** and **2** are compared in Table 2, with the final positional parameters of the non-hydrogen atoms in Tables 3 and 4, respectively.



Scheme 1 (*i*) $Zn(O_2CMe)_2$ + $NaClO_4$ in dry MeOH; (*ii*) $Zn(O_2CMe)_2$ + $NaClO_4$ in hydrous MeOH; (*iii*) water; (*iv*) CH_3CO_2H; (*v*) $NaBH_4$ in MeOH; (*vi*) H_4edta in water + CH_2Cl_2; (*vii*) NH_4PF_6

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses.—The synthesis of all compounds obtained in this study is illustrated in Scheme 1. Each product was obtained in very high yield (> 90%), except for the metal-free condensation product HL^3.

From the kinetic point of view, metal-free Schiff-base condensation of dialdehyde and diamine, in general, affords polymeric Schiff-base products. Even in the case of metal-template reactions, the Schiff-base condensation sometimes

Table 3 Final atomic coordinates for complex **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Zn(1)	0.083 58(7)	0.120 13(5)	0.629 14(2)
Zn(2)	−0.065 16(7)	0.304 66(5)	0.564 92(2)
Cl(1)	0.435 1(2)	0.228 53(12)	0.844 84(5)
Cl(2)	0.617 2(3)	0.162 5(2)	0.182 79(9)
Cl(3)	0.413 9(2)	0.134 6(2)	0.102 21(7)
O(1)	0.034 3(4)	0.283 3(3)	0.629 81(11)
O(2)	0.128 7(4)	−0.059 1(3)	0.651 84(12)
O(3)	0.061 1(5)	−0.248 0(3)	0.579 35(14)
O(4)	−0.190 1(4)	0.367 3(3)	0.496 66(12)
O(5)	−0.133 6(4)	0.077 7(3)	0.620 29(12)
O(6)	−0.232 2(4)	0.198 5(3)	0.569 16(12)
O(7)	0.190 1(4)	0.105 5(3)	0.570 74(12)
O(8)	0.108 5(4)	0.251 6(3)	0.529 72(12)
O(9)	0.428 6(8)	0.336 8(4)	0.831 1(2)
O(10)	0.420 4(7)	0.213 2(7)	0.891 7(2)
O(11)	0.571 2(7)	0.184 6(5)	0.832 3(2)
O(12)	0.307 7(7)	0.173 6(5)	0.824 3(2)
N(1)	0.216 4(5)	0.136 7(3)	0.686 7(2)
N(2)	−0.099 5(5)	0.462 5(3)	0.578 57(14)
C(1)	0.076 9(6)	0.356 8(4)	0.661 3(2)
C(2)	0.028 8(6)	0.468 2(4)	0.655 8(2)
C(3)	0.074 8(7)	0.543 5(4)	0.690 3(2)
C(4)	0.162 7(7)	0.519 0(5)	0.729 0(2)
C(5)	0.208 3(6)	0.412 8(5)	0.733 2(2)
C(6)	0.167 6(6)	0.330 6(4)	0.701 0(2)
C(7)	0.211 5(9)	0.606 3(5)	0.762 9(2)
C(8)	0.232 7(6)	0.223 8(5)	0.710 9(2)
C(9)	0.299 4(7)	0.037 0(5)	0.701 6(2)
C(10)	0.195 3(7)	−0.057 5(5)	0.697 7(2)
C(11)	0.011 3(8)	−0.140 9(5)	0.647 6(2)
C(12)	−0.032 2(8)	−0.165 9(5)	0.598 4(2)
C(13)	−0.057 0(6)	0.512 4(4)	0.615 9(2)
C(14)	−0.173 4(7)	0.530 0(4)	0.541 8(2)
C(15)	−0.276 7(6)	0.459 9(5)	0.511 6(2)
C(16)	−0.276 9(7)	0.301 7(6)	0.463 7(2)
C(17)	0.184 7(7)	−0.208 6(5)	0.553 2(2)
C(18)	−0.243 40(6)	0.118 0(4)	0.596 0(2)
C(19)	−0.397 8(7)	0.066 4(5)	0.599 9(2)
C(20)	0.194 8(6)	0.169 8(5)	0.536 8(2)
C(21)	0.312 9(8)	0.145 9(7)	0.502 0(2)
C(22)	0.521 9(8)	0.073 2(6)	0.146 1(3)

gives different macrocycles depending upon the reaction conditions, *e.g.* [2 + 2] tetra-Schiff base[2a,b] or [3 + 3] hexa-Schiff base[15] macrocycles. In this instance using 2,6-diformyl-4-methylphenol and 1,11-diamino-3,6,9-trioxaundecane, the metal-template reaction where zinc acetate functions as the template core led to quantitative tetra-Schiff-base macrocyclisation giving the tetranuclear zinc complexes **1** and **2**. This preferential [2 + 2] macrocyclisation is clearly favoured by the use of the zinc ion as the template core. In fact, the metal-free (equimolar) Schiff-base condensation gave a [1 + 1] di-Schiff-base macrocycle as its hydrogen hexafluorophosphate salt, $[HL^3][HPF_6]$, which was characterised by NMR and FAB-mass spectroscopies and a preliminary crystal-structure analysis.[16] Furthermore, attempts to prepare the same macrocycle using $M(O_2CMe)_2$ ($M = Cu^{II}$, Ni^{II} or Mn^{II}) as the template core were unsuccessful, giving oily or amorphous products. These discriminating results may be rationally interpreted in terms of the concept of hard and soft acids and bases;[17] zinc(II) ion is categorised as a typical hard acid and thus would have a high affinity for the ether-type oxygen atom, whereas Cu^{II}, Ni^{II} and Mn^{II} would have a poorer affinity for the ether oxygen. In fact, recrystallisation of an amorphous product, obtained from the reaction with manganese(II) acetate, finally gave yellow crystals, whose ^1H NMR and IR spectra were consistent with those of $[HL^3][HPF_6]$.

Reduction of complex **1** (or **2**) with sodium tetrahydroborate gave a complex of the reduced macrocycle $[L^2]^{2-}$, but in the form of dinuclear zinc complex **3**. From complex **3** the metal-free macrocycle H_2L^2 could also be isolated using H_4edta to remove the zinc ions in alkaline solution. The successful isolation of the saturated macrocycle is rather interesting when considering the case of a closely related macrocycle recently reported by Kahwa and co-workers.[18] Their macrocyclic compound, which was prepared by Schiff-base condensation of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dioxaoctane, is also readily reduced to the saturated form.[18b] However, the reduced product, in the metal-free form, is unstable toward atmospheric oxidation, finally giving a partially oxidized amine–imine phenolate macrocycle. On the other hand, macrocycle H_2L^2 is very stable in air and no proof for oxidation of CHNH to C=N was obtained from ^1H NMR spectroscopy even after one month.

Although both H_2L^1 and H_2L^2, which have the same core size, were expected to show similar complexation behaviour toward zinc ion, the former functions as a tetranucleating ligand while the latter acts as a dinucleating one. The structures of the two tetranuclear zinc complexes **1** and **2** have been determined by X-ray analysis and their chemistry in solution has been studied by NMR spectroscopy. The dinuclear zinc complex **3** has been characterised by elemental analysis and spectroscopic methods. These results are described below.

Structural Description of $\mathbf{1}\cdot 2CH_2Cl_2$ *and* **2**.—Yellow needle-like crystals of **1** obtained from a mixture of dry CH_2Cl_2 and MeOH showed remarkable instability in air, probably due to the loss of CH_2Cl_2 molecules from the crystal lattice. In fact, the X-ray diffraction study revealed that the solvent molecules are captured in the lattice together with the cations, $[Zn_4L^1(\mu\text{-}O_2CMe)_4]^{2+}$, and perchlorate anions. The structure of the cation and atom-numbering scheme are presented in Fig. 1. The compound resides on a crystallographically imposed centre of symmetry, relating the primed and unprimed atoms. The macrocycle has a planar form and linear conformation with respect to its polyether chains, producing a large cavity in the centre of the ring, into which four zinc ions are encapsulated as a pair of μ-phenoxo-bis(μ-carboxylato)dizinc species. The two zinc ions in each dinuclear core are at a distance of 3.1588(9) Å, and are crystallographically inequivalent. However, the metal ions have essentially the same co-ordination geometry (distorted trigonal bipyramid) each possessing an NO_4 donor set, *i.e.* bridging phenoxo oxygen [Zn(1)–O(1) 2.039(3), Zn(2)–O(1) 2.044(3) Å], imine nitrogen [Zn(1)–N(1) 1.991(4), Zn(2)–N(2) 1.993(4) Å], acetato oxygen [Zn(1)–O(5) 1.951(3), Zn(1)–O(7) 1.953(4), Zn(2)–O(6) 1.945(4), Zn(2)–O(8) 1.949(4) Å], and the ether oxygen [Zn(1)–O(2) 2.315(3), Zn(2)–O(4) 2.336(3) Å], with the phenoxo and ether oxygen atoms occupying the axial sites. Concerning bond distances, the zinc(II)–imine nitrogen interaction (average 1.992 Å) and all the zinc(II)–oxygen bonds (average 1.980 Å), except for the ether oxygens, fall well within the range of distances observed for typical zinc(II)–nitrogen[2a,19] and –oxygen[20] co-ordination compounds. The bond distances between the $Zn^{II}–O_{ether}$ linkages (average 2.326 Å) are slightly longer than the typical values of 2.2–2.3 Å for zinc(II)–crown ether oxygen interactions.[21]

The structure of the other tetranuclear zinc complex **2** differs significantly from that of **1**, at each dinuclear zinc core of complex **2** there is only one bridging acetate. The structure of the cation of **2** and atom-numbering scheme are presented in Fig. 2, together with the tetranuclear core structure (Fig. 3). One of the bridging acetate groups at each dinuclear zinc core of complex **1** has been replaced by two hydroxo ions in **2**, which further co-ordinate to the other zinc pair thereby linking the two dimer units, yielding a Zn_4O_4 cluster-like ring core (Fig. 3). Unlike the planar form of $[L^1]^{2-}$ in **1**, the two polyether chains of the ligand in **2** are folded and the two dimeric units formed by the phenoxo bridges are paired parallel to each other by π–π

Table 4 Final atomic coordinates for complex **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Zn(1)	0.382 56(14)	0.385 45(6)	0.063 24(14)
Zn(2)	0.504 76(13)	0.404 99(6)	0.320 80(13)
Zn(3)	0.624 3(2)	0.387 78(7)	0.056 28(14)
Zn(4)	0.741 12(13)	0.378 72(6)	0.316 38(13)
Cl(1)*	0.248 9	0.378 0	0.531 2
Cl(2)*	0.338 9	0.187 8	0.811 6
O(1)	0.443 4(7)	0.355 9(3)	0.210 6(7)
O(2)	0.263 7(10)	0.401 8(4)	−0.119 2(10)
O(3)	0.399 6(12)	0.472 5(4)	−0.125 5(12)
O(4)	0.576 2(9)	0.427 0(4)	−0.104 4(8)
O(5)	0.672 9(7)	0.343 9(3)	0.177 1(7)
O(6)	0.864 2(8)	0.404 1(4)	0.506 7(8)
O(7)	0.763 3(8)	0.482 9(4)	0.462 0(9)
O(8)	0.584 0(7)	0.451 6(3)	0.486 3(7)
O(9)	0.636 7(7)	0.418 7(3)	0.312 7(7)
O(10)	0.502 3(7)	0.414 9(3)	0.059 8(7)
O(11)	0.287 3(8)	0.426 1(4)	0.090 6(8)
O(12)	0.377 9(8)	0.443 5(3)	0.260 5(7)
O(13)	0.762 3(8)	0.419 7(4)	0.111 9(8)
O(14)	0.846 2(7)	0.410 9(3)	0.289 5(7)
O(15)*	0.840 1	0.087 9	0.601 7
O(15a)*	0.344 3	0.369 8	0.634 6
O(16)*	0.791 5	0.167 2	0.567 7
O(16a)*	0.210 9	0.347 8	0.580 4
O(17)*	0.752 0	0.128 2	0.436 0
O(17a)*	0.269 5	0.335 0	0.483 1
O(18)*	0.643 3	0.102 5	0.516 9
O(18a)*	0.699 2	0.102 8	0.428 1
O(19)*	0.367 0	0.179 9	0.932 7
O(19a)*	0.388 9	0.143 5	0.845 6
O(20)*	0.454 8	0.184 4	0.814 3
O(20a)*	0.376 3	0.239 9	0.805 7
O(21)*	0.290 4	0.146 5	0.752 6
O(21a)*	0.225 2	0.200 8	0.707 4
O(22)*	0.269 1	0.227 2	0.764 0
O(22a)*	0.286 8	0.211 7	0.865 0
N(1)	0.335 2(10)	0.329 3(4)	−0.013 4(9)
N(2)	0.519 8(9)	0.367 6(4)	0.440 0(8)
N(3)	0.598 7(10)	0.339 4(5)	−0.051 7(10)
N(4)	0.776 5(9)	0.324 9(4)	0.407 8(9)
C(1)	0.478(2)	0.176 1(6)	0.298(2)
C(2)	0.464 9(11)	0.225 3(6)	0.268 5(13)
C(3)	0.422 7(12)	0.239 5(5)	0.166 0(12)
C(4)	0.413 0(11)	0.283 6(5)	0.149 8(12)
C(5)	0.448 8(10)	0.314 8(5)	0.232 2(11)
C(6)	0.487 6(11)	0.300 6(5)	0.339 2(11)
C(7)	0.494 9(11)	0.254 1(6)	0.354 1(13)
C(8)	0.357 2(12)	0.293 2(6)	0.031 8(13)
C(9)	0.284(2)	0.327 5(7)	−0.131 4(14)
C(10)	0.206(2)	0.362 8(7)	−0.172(2)
C(11)	0.228(2)	0.447 0(11)	−0.161(2)
C(12)	0.297(3)	0.473(2)	−0.194(3)
C(13)	0.445(2)	0.484 7(8)	−0.195 9(13)
C(14)	0.554(2)	0.472 5(7)	−0.125(2)
C(15)	0.553(3)	0.404 3(8)	−0.188(2)
C(16)	0.564(2)	0.357 8(9)	−0.171 5(13)
C(17)	0.600 4(13)	0.298 9(6)	−0.034 5(13)
C(18)	0.648(2)	0.159 8(6)	0.139(2)
C(19)	0.654 6(11)	0.208 6(5)	0.143 1(13)
C(20)	0.695 8(11)	0.226 8(5)	0.246 1(14)
C(21)	0.706 1(10)	0.272 4(6)	0.258 1(12)
C(22)	0.670 6(10)	0.303 1(5)	0.167 9(11)
C(23)	0.630 9(11)	0.277 4(6)	0.066 8(12)
C(24)	0.625 3(11)	0.234 9(5)	0.056 9(13)
C(25)	0.758 0(10)	0.287 7(6)	0.375 2(12)
C(26)	0.827 0(14)	0.330 0(6)	0.528 7(12)
C(27)	0.914 3(14)	0.366 6(7)	0.565 8(14)
C(28)	0.933 4(14)	0.439 0(6)	0.555(2)
C(29)	0.873 1(13)	0.478 4(8)	0.481 4(14)
C(30)	0.753 5(12)	0.493 7(6)	0.556 1(11)
C(31)	0.625 2(12)	0.493 3(6)	0.506 6(12)
C(32)	0.629 7(14)	0.425 0(6)	0.575 7(13)
C(33)	0.539(2)	0.387 3(7)	0.542 7(12)
C(34)	0.513 3(11)	0.326 7(6)	0.434 5(11)
C(35)	0.298 4(12)	0.444 7(5)	0.177 6(11)
C(36)	0.198 8(13)	0.473 6(7)	0.157 7(15)
C(37)	0.841 3(11)	0.422 5(5)	0.201 7(12)
C(38)	0.943 7(12)	0.441 9(7)	0.207 1(13)

* Positions of these atoms were fixed at the final stage of refinement.

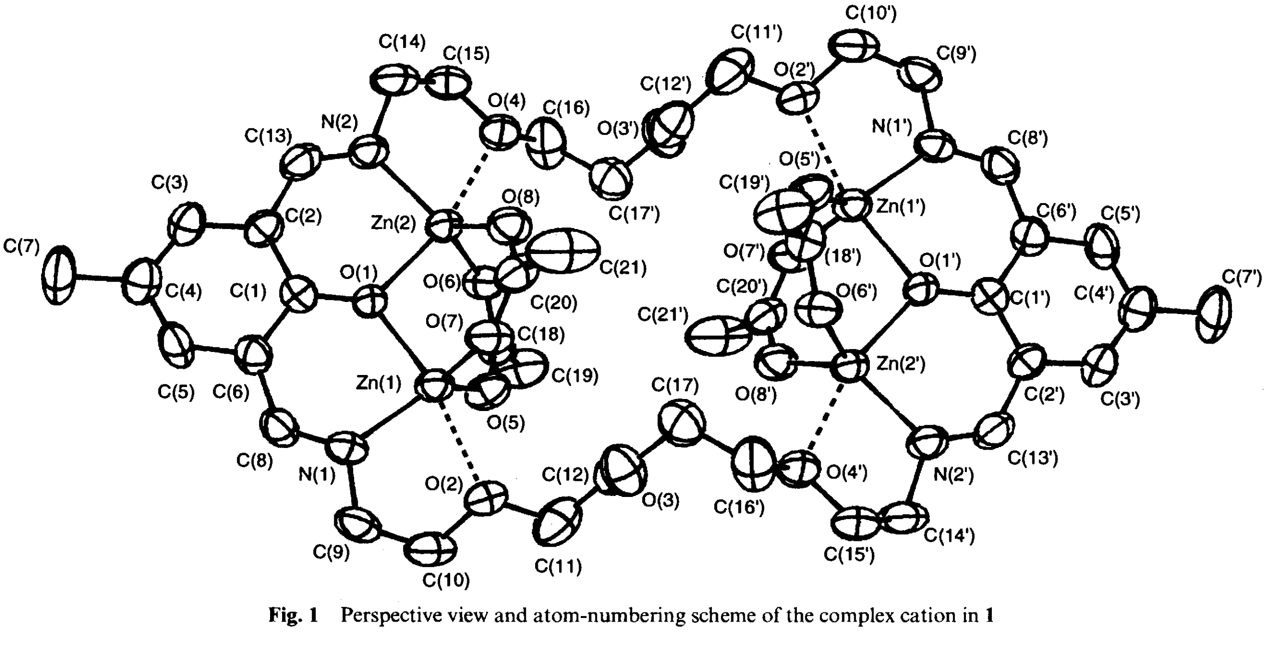


Fig. 1 Perspective view and atom-numbering scheme of the complex cation in **1**

stacking of two phenolate rings at a distance of *ca.* 3.4 Å, which may contribute to the close proximity of the two dimeric units, finally yielding the bis-μ-hydroxo dimer pair. In this compound the four zinc ions are crystallographically inequivalent, while their co-ordination geometry is trigonal bipyramidal consisting of NO_4 donor sets with the phenoxo and ether oxygens being in

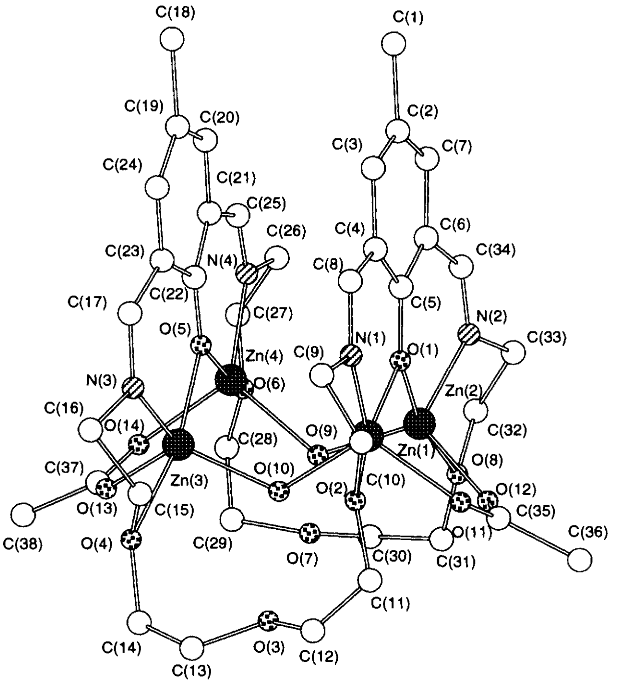


Fig. 2 Perspective view and atom-numbering scheme of the complex cation in **2**

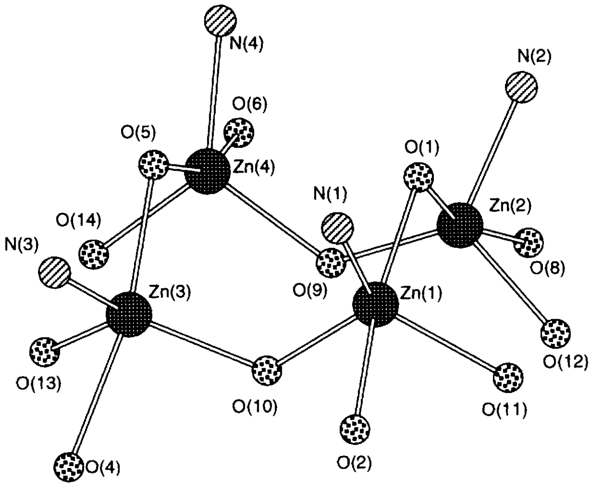


Fig. 3 Co-ordination geometries of the four zinc ions in complex **2**

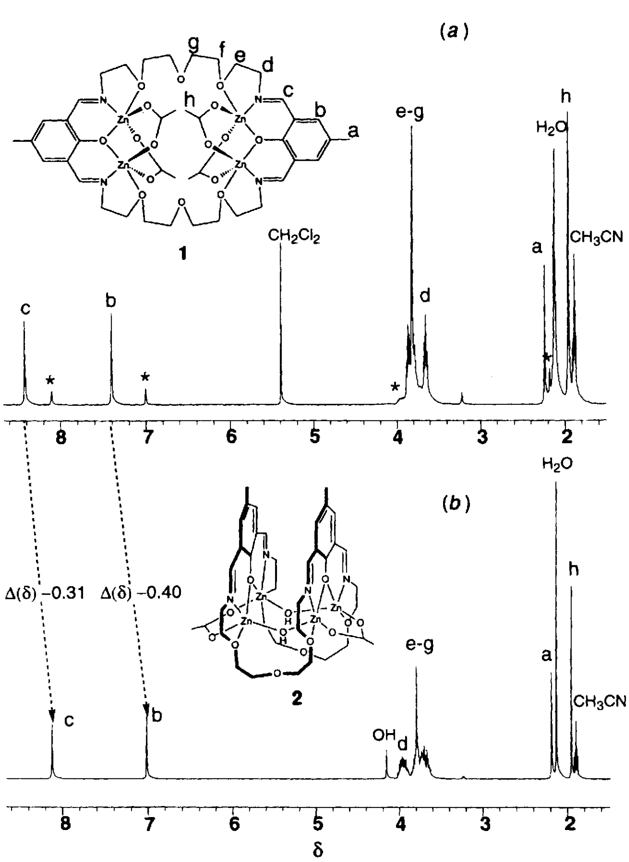
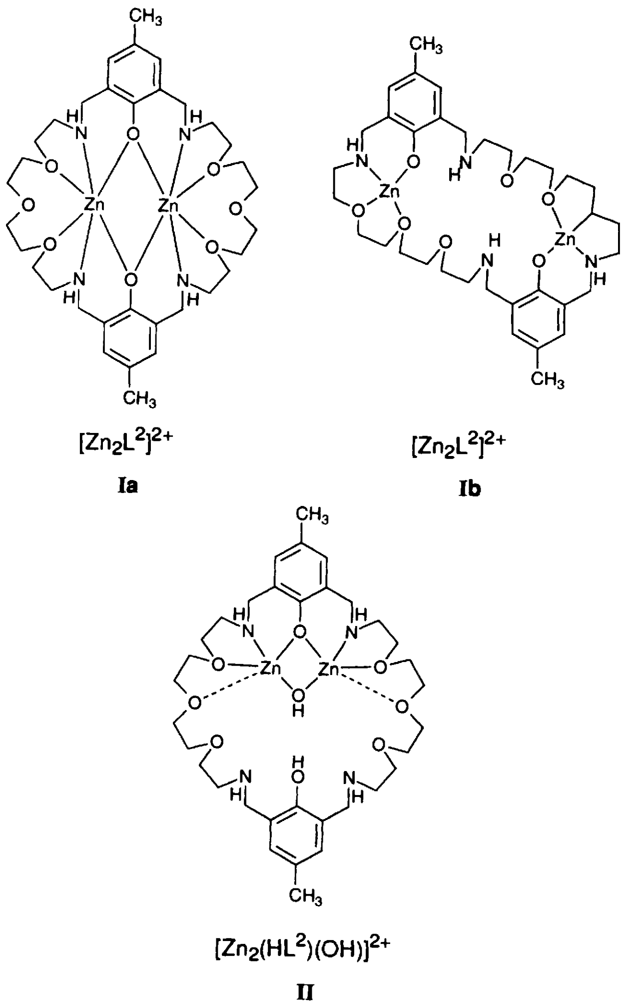


Fig. 4 Proton NMR spectra of (*a*) complex **1** and (*b*) complex **2** in CD_3CN; * complex **2** (converted from **1** by water in the solvent used, see text)

axial positions, as is also the case in **1**. Although the $Zn^{II}-O_{ether}$ bonds (average 2.43 Å) are longer than those observed in **1**, all other bond distances are close to those of the corresponding ones in **1** (see Table 2 for their comparison). Owing to the poor quality of the crystal and the limited number of reflections, two water molecules in **2** could not be located by X-ray analysis and yet their presence had been predicted from elemental analysis. The failure to find these water molecules is reflected in the relatively high *R* value (0.0861) and large thermal parameters and deviations from ideal bond distances and angles for some atoms. However, NMR spectroscopy (^1H and ^{13}C) of **2** in solution supported the vent-stacking structure shown in Fig. 2 and indicated that this structure is maintained in solution, see below.

Solution Structures of **1** *and* **2** *and their Interconversion.*—The molar conductance of complexes **1** (289 S cm^2 mol^{-1}) and **2** (288 S cm^2 mol^{-1}) measured in acetonitrile fall within the range reported for a 1 : 2 electrolyte,[22] suggesting that the structures of both cations as seen in the solid are intact in solution. Additional proof of the retention of the solid-state structure in both cations was obtained from ^1H and ^{13}C NMR spectroscopy in CD_3CN. Proton NMR spectra of **1** and **2** are compared in Fig. 4, and all signals from each compound can be reasonably assigned. The most pronounced difference in the chemical shifts of the macrocycles of the two compounds is observed in the region of the imine and phenolate ring protons. The chemical shifts of the imine protons (δ 8.43) and the ring protons (δ 7.42) in the spectrum of **1** are shifted to δ 8.12 and 7.02, respectively, in the spectrum of **2**. This upfield shift can be regarded as proof of the stacking interaction between the two phenolate rings observed in the solid structure of **2**. Furthermore, both compounds **1** and **2** gave twelve resonances in their ^{13}C NMR spectra in the same solvent, excluding the solvent peaks. This number of resonances can be explained by recognising that both compounds have very high symmetry in their solution structures, probably D_{2h} for **1** and C_{2v} for **2** on the NMR time-scale. Thus we conclude that, in solution, compounds **1** and **2** retain their respective planar and vent-stacking forms seen in the solid state.

Compounds **1** and **2** could be selectively isolated by the subtle difference in the solvent used, *i.e.* the use of dry methanol preferentially gave **1** and hydrous methanol gave **2**. This result suggests that **1** and **2** are interchangeable in solution, depending upon conditions, *e.g.* water content in the solvent used. In fact, addition of one drop of D_2O to a saturated solution of **1** in CD_3CN changed its ^1H NMR spectrum to that of **2**. Furthermore, a similar titration experiment using acetic acid with compound **2** showed reversion to **1**, which was also confirmed by ^1H NMR spectroscopy. Thus, we conclude that interconversion between **1** and **2** occurs readily in solution, depending on the presence of water or acetic acid.


$[Zn_2L^2]^{2+}$
Ia
$[Zn_2L^2]^{2+}$
Ib
$[Zn_2(HL^2)(OH)]^{2+}$
II

Scheme 2 Possible structures for complex **3**

Characterization of the Dinuclear Zinc Complex **3**.—Direct reduction of complex **1** (or **2**) afforded the zinc complex **3**, which contained the reduced macrocycle $[L^2]^{2-}$ whose metal-free form was subsequently isolated by demetallation procedures. Complete reduction of $[L^1]^{2-}$ to $[L^2]^{2-}$ was inferred from the disappearance of the yellow colour in the reaction mixture and confirmed by ^1H and ^{13}C NMR spectroscopy for the isolated complex **3** and by FAB mass and ^1H NMR spectroscopy for the metal-free macrocycle.

Attempts to obtain single crystals of **3** suitable for an X-ray diffraction study have so far been unsuccessful. However, its elemental analysis (C, H, N and Zn) indicates that the complex is a dinuclear species which can be formulated as $[Zn_2L^2][ClO_4]_2 \cdot H_2O$ (**I**) or $[Zn_2(HL^2)(OH)][ClO_4]_2$ (**II**). Scheme 2 illustrates two plausible structures for **I** and one for **II**. Routine NMR spectroscopy gave conclusive evidence for the structural assignment. The ^{13}C NMR spectrum of **3** measured in CD_3CN exhibited only ten signals for this compound, showing high symmetry for the structure in solution. Of the three candidates, structure **Ia** has the highest symmetry, in which a quarter of the molecule is regarded as a structurally asymmetric unit, meaning that ten carbon atoms from the macrocycle are chemically and magnetically independent. On the other hand, 20 carbons from the half unit are expected to be independent for structures **Ib** and **II** with lower symmetry. Although some other structural analogues are indeed expected for this compound, the appearance of only ten signals in the ^{13}C NMR spectrum concludes that complex **3** has the structure **Ia** in solution.

Conclusion

The new tetra-Schiff-base type of macrocycle, H_2L^1, has a cavity large enough to accommodate two μ-phenoxo dizinc(II) cores exhibiting different structural features, namely: planar form for **1** and vent-stacking form for **2**. Interestingly, these two complexes rapidly interconvert in solution depending upon the content of water or acetic acid. These results clearly indicate that the macrocyclic ring is very flexible. From the viewpoint of structural chemistry, stacking interaction between two phenolate rings as seen in complex **2** undoubtedly contributes to drawing the two μ-phenoxo zinc pairs closer to each other. Utilisation of such a stacking interaction may be potentially useful in the assembly of several metal ions when designing polynuclear metal complexes aimed at modelling the active sites of polynuclear metalloenzymes, *e.g.* the Mn_4 cluster of OEC in photosystem II.[4] Despite being a Zn^{II} complex, the structure of **2** has some relevance to OEC as recent theoretical studies, from magnetic chemistry[23] and molecular orbital theory,[24] suggested a ring arrangement for the four Mn ions in which hydroxo or oxo anions, the source of dioxygen release, are facing each other.

Unfortunately, attempts to synthesize tetranuclear manganese complexes with the same procedure as that described for compounds **1** and **2** were unsuccessful, giving the [1 + 1] condensation product in a metal-free form, probably due to the poorer affinity of the manganese ion for the ether oxygen atoms. To obtain tetra- or poly-nuclear transition-metal complexes, with potential application to multi-electron redox catalysis, several functional groups with co-ordinating ability should be introduced onto these macrocyclic ligands. Such a study is now in progress in our laboratory.

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