DALTON

Syntheses and characterization of novel tri- and hexa-nuclear zinc complexes with biomimetic chelate ligands

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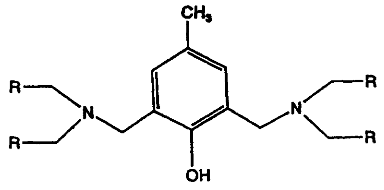
Reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ with pentadentate 1,3-bis(salicylidenamino)propan-2-ol (H_2hsalpn) and the tridentate 4-methyl-2,6-bis(morpholinomethyl)phenol (Hbmmp) yielded the trinuclear zinc complex $[Zn_3(O_2CPh)_2(hsalpn)_2]{\cdot}2MeOH$ **1** and the hexanuclear zinc compound $[Zn_6(OH)_6(bmmp)_3][ClO_4]_3$ **2**. The complexes were characterized by single-crystal X-ray diffraction analyses. Both structures were solved using direct methods and refined on *F* by full-matrix least squares. Complex **1** consists of one central zinc ion which is octahedrally co-ordinated and two terminal metals surrounded by five donor atoms in the form of a square pyramid. The left and right wing zinc ions are connected to the central metal atom *via* two phenolate oxygens of the dinucleating ligand and the oxygens of the benzoate ion. The six equivalent tetrahedrally co-ordinated zinc ions in **2** are arranged in form of a regular trigonal prism. Three dinuclear subunits are connected to each other by hydroxide groups. Both compounds display a new type of structure for homotri- and homohexa-nuclear zinc complexes.

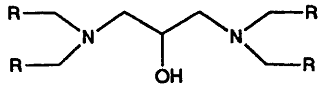
The Zn^{2+} ion is of essential importance in several biological processes.[1] In recent years there has been a growing interest in enzymes with more than one zinc atom in the active site, for example phospholipase C (PLC)[2] and nuclease P1 (NP1).[3] Crystal structure analyses show three zinc atoms in the active site, of which two are connected by a bridging hydroxide group or water molecule and an additional carboxylate function. The metal–metal separation is 3.3 Å. The third zinc is located somewhat apart from this dinuclear unit. Despite its well developed co-ordination chemistry, little is known about dinuclear zinc compounds which can act as structural or functional models for biological systems.[4–7]

One type of polydentate donor molecule used for the stabilization of dinuclear metal complexes (dinucleating ligands) contain a phenol (**A**) or alkanol unit (**B**) which when deprotonated bridges two metal centres. In addition they contain up to six other nitrogen or oxygen donor atoms. These systems display one severe disadvantage. They provide four donor atoms for each metal and almost saturate those with no requirement for six ligands. With additional bidentate groups like carboxylate or phosphate the resulting co-ordination spheres are often even more saturated.[5,6] Therefore a water molecule,[1] very important for the biological processes in zinc enzymes, will not find a vacant co-ordination site at which to bind to the metal ion.

As part of our systematic study[5–7] we reduced the number of potential donor atoms in dinucleating ligands to five and three (although the central bridging alkanol or phenol units are retained). Furthermore, we did not use additional bidentate bridging ligands in order to get 'free' co-ordination sites for solvent molecules. In the present investigation the pentadentate 1,3-bis(salicylidenamino)propan-2-ol (H_2hsalpn) and the tridentate 4-methyl-2,6-bis(morpholinomethyl)phenol (Hbmmp) are used. Both form metal compounds with dinuclear units (H_2hsalpn, refs. 8–18; Hbmmp, ref. 19). However, the resulting zinc complexes do not exhibit the structural features known from the literature but have new types of metal arrangements. Here we report details on the synthesis, structural characterization and spectroscopic properties of the trinuclear zinc complex $[Zn_3(O_2CPh)_2(hsalpn)_2]{\cdot}2MeOH$ **1** and of the hexanuclear zinc compound $[Zn_6(OH)_6(bmmp)_3][ClO_4]_3$ **2**.



A



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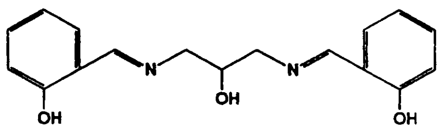
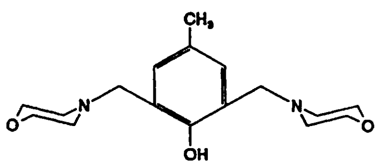


H_2hsalpn



Hbmmp

Results and Discussion

Synthesis of the complexes

The compound H_2hsalpn is easily accessible by a reaction between 1,3-diaminopropan-2-ol and salicylaldehyde;[12a]

Hbmmp can be obtained by a Mannich reaction between *p*-cresol, formaldehyde and morpholine.[19] The complex $[Zn_3(O_2CPh)_2(hsalpn)_2]\cdot 2MeOH$ **1** is formed by reaction of $Zn(ClO_4)_2\cdot 6H_2O$, $H_2hsalpn$ and sodium benzoate in methanol, $[Zn_6(OH)_6(bmmp)_3][ClO_4]_3$ **2** by reaction of $Zn(ClO_4)_2\cdot 6H_2O$ with Hbmmp in a methanol–ethanol mixture. The structures of both complexes were determined by single-crystal X-ray diffraction studies. The formulas of **1** and **2** are in agreement with their elemental analyses.

Molecular structure of $[Zn_3(O_2CPh)_2(hsalpn)_2]\cdot 2MeOH$ 1

Fig. 1 gives a perspective view of the complex molecule in **1** together with the atomic labelling system. The geometry of the central trinuclear unit is shown in Fig. 2. Selected interatomic distances and angles, with their estimated standard deviations (e.s.d.s), are collected in Table 1. The neutral compound **1** consists of two Zn(hsalpn) units connected to each other by a completely encapsulated third zinc ion which is located on a crystallographic inversion centre. The cage of this central zinc atom is formed by two phenolate bridges, O(2) and O(3), from each Zn(hsalpn) moiety and by two benzoato functions that furthermore connect the central with the two outermost metal ions resulting in an octahedral environment for Zn(2). The co-ordination geometry around this central zinc ion displays only slight distortions. The bond distances are relatively similar with values of 2.139(2) [Zn(2)–O(2)], 2.092(2) [Zn(2)–O(3)] and 2.121(2) Å [Zn(2)–O(5)]. The greatest deviation of the bond angles from those of an ideal geometry is found for O(2)–Zn(2)–O(3) with 77.3(1)° and O(3)–Zn(2)–O(2a) with 102.7(1)°. All other bond angles are close to their ideal 90 and 180° values.

Complex **1** is one of the few examples stabilized by a biomimetic chelate ligand with different co-ordination numbers for the same type of metal ion within one molecule.[5,13] The left and right wing zinc ions in this trinuclear compound are co-ordinated by the two nitrogen and phenoxy donors of each Zn(hsalpn) unit and one oxygen of the bridging benzoato group resulting in square-pyramidal co-ordination polyhedra. The substantial distortion of the square pyramids is revealed by the bond angles between apical and equatorial donor atoms, O(4)–Zn(1)–N(1) 102.9(1), O(4)–Zn(1)–N(2) 104.0(1), O(4)–Zn(1)–O(2) 99.1(1) and O(4)–Zn(1)–O(3) 101.3(1)°. The average of these bond angles is approximately 11.8° greater than the 90° angle in a regular square pyramid. The bond angles between the donor atoms in equatorial positions exhibit values of 80.8(1) [O(2)–Zn(1)–O(3)], 88.6(1) [O(3)–Zn(1)–N(2)], 90.9(1) [N(1)–Zn(1)–N(2)] and 89.9(1)° [O(2)–Zn(1)–N(1)], *i.e.* there is less distortion in this direction. A similar pattern can be found in the bond distances. The distance between Zn(1) and the apical donor O(4) is with 1.983(3) Å, significantly shorter than the average bond distance between Zn(1) and the equatorial donors (2.052 Å). This atom is displaced 0.432 Å out of the least-squares plane defined by the equatorial donor atoms in the direction of the oxygen of the benzoate moiety.

The question arises as to whether the co-ordination polyhedron around Zn(1) can be described as a distorted square pyramid or a distorted trigonal bipyramid. Further information can be obtained by determining the structural index τ[20] which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$); $\tau = (\beta - \alpha)/60°$, α and β being the two largest angles around the central atom. The value of τ is 0.015 for Zn(1). The co-ordination geometry of the outermost zinc ions in this complex is therefore indeed best described as a distorted square pyramid. For the equatorial ligands in this polyhedron the average deviation from their least-squares plane was calculated to be just 0.012 Å, indicating the high planarity of this unit. The greater distortion of the co-ordination geometry around the outermost zinc atoms in comparison to the central one is attributed to the steric effects of the chelate ligand.

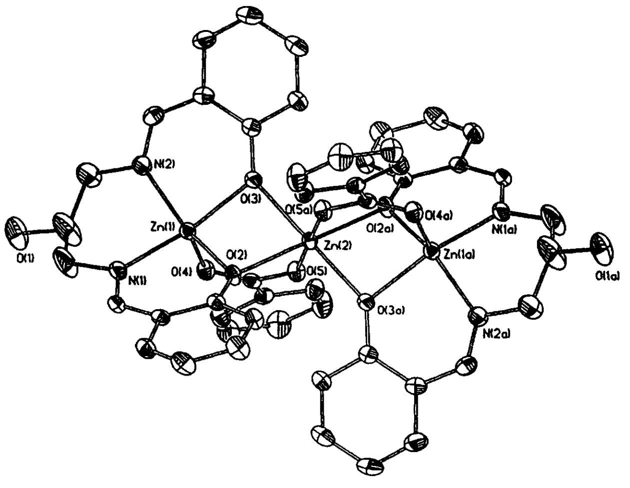


Fig. 1 Molecular structure and atomic numbering scheme for $[Zn_3(O_2CPh)_2(hsalpn)_2]$ in **1**. Ellipsoids are drawn at the 50% probability level

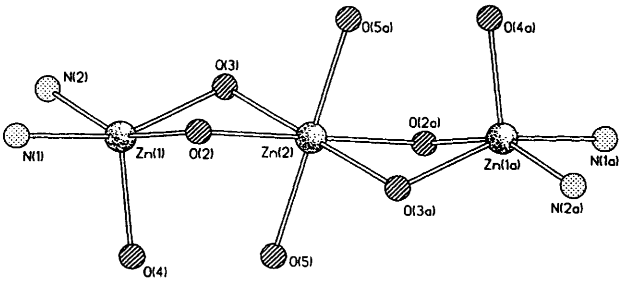


Fig. 2 Inner co-ordination sphere for the zinc ions in complex **1**

Table 1 Selected interatomic distances (Å) and angles (°) for complex **1**

Zn(1)···Zn(2)	3.064(1)		
Zn(1)–O(2)	2.029(2)	Zn(1)–O(3)	2.048(2)
Zn(1)–O(4)	1.983(3)	Zn(1)–N(1)	2.065(2)
Zn(1)–N(2)	2.064(3)	Zn(2)–O(2)	2.139(2)
Zn(2)–O(3)	2.092(2)	Zn(2)–O(5)	2.121(2)
O(2)–Zn(1)–O(3)	80.8(1)	O(2)–Zn(1)–O(4)	99.1(1)
O(2)–Zn(1)–N(1)	89.9(1)	O(2)–Zn(1)–N(2)	156.1(1)
O(3)–Zn(1)–O(4)	101.3(1)	O(3)–Zn(1)–N(1)	155.2(1)
O(3)–Zn(1)–N(2)	88.6(1)	O(4)–Zn(1)–N(1)	102.9(1)
O(4)–Zn(1)–N(2)	104.0(1)	N(1)–Zn(1)–N(2)	90.9(1)
O(2)–Zn(2)–O(3)	77.3(1)	O(2)–Zn(2)–O(5)	89.9(1)
O(2)–Zn(2)–O(2a)	180.0	O(2)–Zn(2)–O(3a)	102.7(1)
O(2)–Zn(2)–O(5a)	91.1(1)	O(3)–Zn(2)–O(5)	86.3(1)
O(3)–Zn(2)–O(2a)	102.7(1)	O(3)–Zn(2)–O(3a)	180.0
O(3)–Zn(2)–O(5a)	93.7(1)	O(5)–Zn(2)–O(5a)	180.0

The oxygen atom O(1), which usually bridges two metal centres,[8,9,10b–12b,14b,16] is in this case not involved in metal co-ordination. It is protonated and can be found at the periphery of the neutral molecule. The position of the corresponding hydrogen atom H(1) could be located in the Fourier-difference map and was refined isotropically. Besides the normal bridging mode, there are two other complexes in which, as in **1**, the alkoxo-oxygen atom is not co-ordinated: a mononuclear manganese(III) complex[18] and a heterotrinuclear Mn_2Na compound with a ligand arrangement comparable to that in **1**.[15a] However, in the latter molecule all three metals are octahedrally co-ordinated.

A structural environment very similar to that in complex **1** is found in another heterotrinuclear complex, $[Zn\{(\mu\text{-}O_2CMe)(salpn\text{-}\mu\text{-}O,O')Cu\}_2]$.[21] The two terminal square-

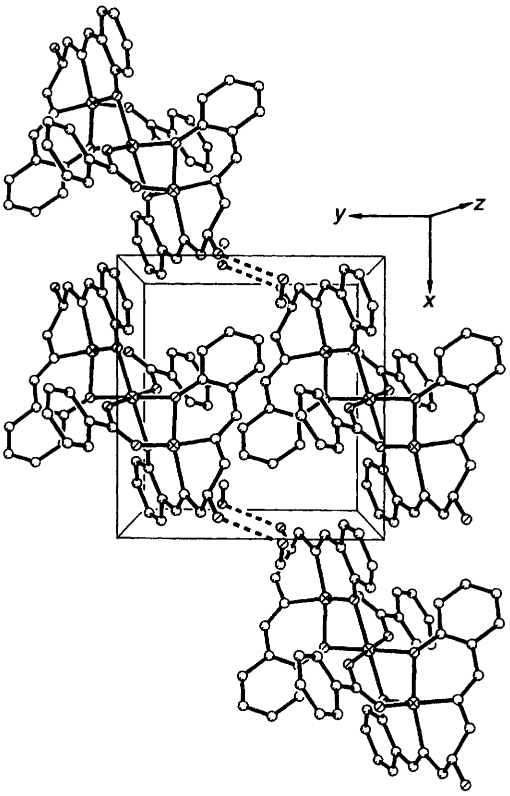


Fig. 3 Packing diagram of complex 1. The hydrogen bonds between the methanol molecules and alcohol hydrogen atoms of the complex are indicated with broken lines

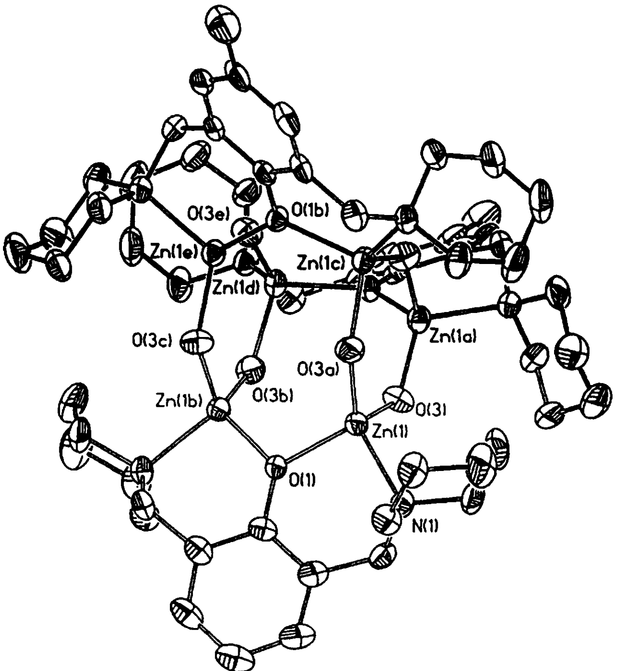


Fig. 4 Molecular structure and atomic numbering scheme for [Zn$_6$(OH)$_6$(bmmp)$_3$][ClO$_4$]$_3$ 2. Ellipsoids are drawn at the 50% probability level

pyramidally co-ordinated copper(II) ions in this compound are connected to the central octahedrally co-ordinated zinc metal through acetato groups and the deprotonated phenoxy moieties of the ligand. The high similarity between this structure and that of 1 is caused by the fact that almost identical ligands were used and that Cu^{II} also prefers a co-ordination number of five.

Table 2 Selected interatomic distances (Å) and angles (°) for complex 2

Zn(1)···Zn(1a)	3.523(1)	Zn(1)···Zn(1b)	3.291(1)
Zn(1)···Zn(1c)	3.523(1)	Zn(1)···Zn(1d)	4.932(2)
Zn(1)···Zn(1e)	4.666(2)		
Zn(1)–O(1)	1.981(3)	Zn(1)–O(3)	1.937(5)
Zn(1)–O(3a)	1.903(5)	Zn(1)–N(1)	2.063(5)
O(1)–Zn(1)–O(3)	105.1(1)	O(1)–Zn(1)–O(3a)	118.8(1)
O(1)–Zn(1)–N(1)	97.3(2)	O(3)–Zn(1)–O(3a)	106.3(2)
O(3)–Zn(1)–N(1)	108.6(2)	N(1)–Zn(1)–O(3a)	119.6(1)

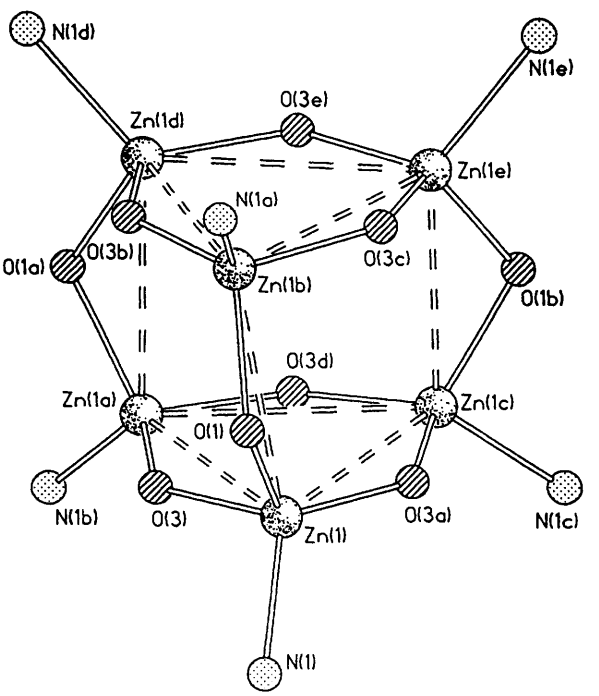


Fig. 5 The core of complex 2 emphasizing the regular trigonal-prismatic arrangement of the zinc ions

The ligand does not have a hydroxy group in the propane backbone, however although H_2hsalpn has such a potential donor group it is not involved in co-ordination in 1. The close equivalence between the two structures is also confirmed by almost identical metal–metal distances, Cu···Zn 3.038(2) and Zn···Zn 3.064(1) Å. These relatively short distances are probably caused by the two phenolato bridges between the outermost and the central metal ion. It also stresses the enormous flexibility of benzoato bridges in homonuclear zinc complexes allowing metal–metal separations between 3.064(1) Å (in 1) and 3.443(3) Å.[5] It is noteworthy that in the structurally similar heterotrinuclear Mn_2Na compound the Mn···Na distance [3.297(1) Å] is significantly longer.[15a]

The intramolecular distances indicate a rather strong hydrogen bond between the oxygen atom of the methanol solvent molecule (OMe) and the hydrogen atom of O(1) [OMe···O(1) 2.753(5), OMe···H(1) 2.13(5) Å]. This hydrogen bond is shown in the packing diagram (Fig. 3).

Complex 1 represents a new structural type of homotrinuclear zinc complex. The only other known trinuclear zinc compounds consist of three zinc ions co-ordinated by a mononucleating ligand. The metal atoms are linked by carbonato groups[22,23] or by an acetato moiety of the ligand.[24]

Molecular structure of [Zn$_6$(OH)$_6$(bmmp)$_3$][ClO$_4$]$_3$ 2

A perspective view of complex 2 is depicted in Fig. 4 together with the atomic labelling system. The geometry of the central hexanuclear cluster emphasizing the regular trigonal-prismatic arrangement of the metal atoms is shown in Fig. 5. Selected interatomic distances and angles are given in Table 2.

Compound **2** can be described as a hexanuclear zinc complex with three identical dinuclear subunits which consist of two metal ions, two hydroxy groups and one bmmp$^-$ ligand. The two zinc atoms within one subunit are bridged by O(1) of the deprotonated phenol group. The tetrahedral co-ordination geometry for each metal is completed by the morpholine nitrogen atom and by two hydroxy units which form the connection to the other subunits resulting in an equivalent NO$_3$ donor set for each zinc ion. The phenoxy bridge is symmetric because O(1) is located on the two-fold axis on which C(1), C(4) and C(5) are also positioned. At 1.981(3) Å the Zn(1)–O(1) distance is in the range typically found for other phenoxo-bridged dinuclear zinc systems.[5,7] The distances between the metal and the two bridging hydroxy-oxygen atoms differ only slightly [1.937(5), Zn(1)–O(3); 1.903(5) Å, Zn(1)–O(3a)]. A value of 2.063(5) Å was found for the distance between the zinc atom and the morpholine N-donor. The distortion of the tetrahedral environment around each metal indicated by these distances is confirmed by the bond angles ranging from 97.3(2) [O(1)–Zn(1)–N(1)] to 119.6(1)° [N(1)–Zn(1)–O(3a)]. This distortion is again caused by the steric effects of the small chelate ligand. Atoms Zn(1), Zn(1a), Zn(1c), O(3), O(3a) and O(3d) form a distorted six-membered chelate ring. The corresponding angles are significantly different from the 120° angle in a perfect hexagon: O(3)–Zn(1)–O(3a) 106.3(2)° and Zn(1)–O(3)–Zn(1a) 133.1(2)°. Least-squares calculations showed that the hydroxy oxygen atoms are displaced by 0.104 Å out of the plane formed by the three zinc ions Zn(1), Zn(1a) and Zn(1c) in direction of the periphery of the cation. The six metal atoms are arranged in a regular trigonal-prismatic configuration. The phenoxy atoms O(1), O(1a) and O(1b) are located above the edges built by two rectangular faces of the prism, while the hydroxy oxygen atoms are positioned above the edges formed by the trigonal and rectangular faces. At each corner of the prism is a bond in the direction of its periphery towards a morpholine nitrogen atom of the ligand bmmp$^-$.

The zinc–zinc separation for the two metals within one dinuclear subunit is 3.291(1) Å. The distance between two zinc atoms of different subunits bridged by a hydroxide group is significantly larger [3.523(1) Å]. The distances between two zinc ions that are not directly connected to each other by hydroxy units were found to be 4.666(2) [Zn(1) ··· Zn(1e)] and 4.932(2) Å [Zn(1) ··· Zn(1d)]. The morpholine moieties of the ligand bmmp$^-$ are in their energetically stable chair conformation. Owing to the twisting of the central Zn(1)–O(1)–Zn(1b) plane against the aromatic ring (dihedral angle = 55.6°), the morpholine groups are located in *trans* positions towards the central phenolate. The intermolecular distances reveal a hydrogen bond between the hydroxy-oxygen atom O(3) and the oxygen atom O(7) of the perchlorate anion [O(3) ··· O(7) 2.80(3) Å]. The corresponding distance between O(7) and the hydrogen atom H(3), which was found in Fourier-difference maps and afterwards refined isotropically, is 2.08(9) Å. A packing diagram of the structure is shown in Fig. 6.

Complex **2** is the first known hexanuclear zinc complex with a biomimetic ligand in which the metal ions are arranged in the form of a trigonal prism. A hexanuclear copper(II) compound with the central atoms in a distorted trigonal antiprism resulting in a propeller-like structure for the copper ions is mentioned in the literature.[25]

Although dinucleating ligands have been used for the stabilization of complexes **1** and **2**, neither of these compounds can be described as a typical dinuclear complex. The systematic reduction of the number of potential donor atoms in these two ligands to five and three does not lead to the expected dinuclear metal complexes in which the zinc ions bind additional solvent molecules in order to fill their co-ordination spheres. Instead they form species with higher nuclearity.

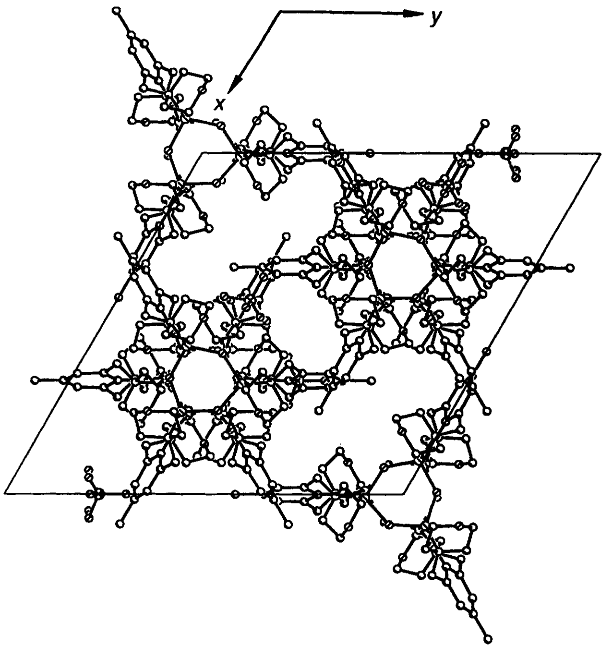


Fig. 6 Packing diagram of complex **2**. Projection of one half of the cell parallel to the *c* axis

Spectroscopic studies

In the infrared powder spectra of complexes **1** and **2** the characteristic bands of the organic ligands hsalpn^{2-} and bmmp$^-$ are the most prominent features. In addition the spectrum of **1** exhibits two strong absorptions at 1590 and 1450 cm^{-1} caused by the asymmetric and the symmetric stretching vibrations of the CO$_2$ unit of the benzoate group. The difference of 140 cm^{-1} between these two frequencies confirms the bidentate bridging co-ordination mode of the carboxylato moiety. The benzoate function also exhibits absorptions at 720 and 680 cm^{-1} which are characteristic for a monosubstituted benzene ring. No significant shift of the ν(C=N) band of free H$_2$hsalpn or Hbmmp is observed upon complexation. In both spectra the absorption is at *ca.* 1630 cm^{-1}. For **2** the co-ordination of the morpholine nitrogen results in a decrease of the N–C stretching frequency of this group from 1260 to 1250 cm^{-1}. The IR spectrum also contains a strong band at 1100 cm^{-1} which is caused by the perchlorate anion. There are two bands in the far IR spectra for both complexes at *ca.* 330 and *ca.* 225 cm^{-1} which we assign to ν(C–O) and ν(C–N) vibrations, respectively.

The proton NMR spectra for complexes **1** and **2** display a shift in the signals of up to 0.4 ppm towards higher fields in comparison to those of the free pro-ligands. The resonances at δ 3.31 (for H$_2$hsalpn) and 2.80 (for Hbmmp) in the NMR spectra of the latter do not show up in the corresponding spectra of the complexes, indicating deprotonation of the phenol units. Furthermore, the spectrum of **1** confirms that the alkanol is still protonated. The only difference observed is a shift of this signal from δ 5.20 for the free H$_2$hsalpn to δ 5.35 for **1**. The signals at δ 7.94, 7.73 and 7.35 can be assigned to the benzoate moiety in **1**.

Experimental

Materials and methods

All reagents were obtained from commercial sources and used as received. Infrared spectra in the range 4000–200 cm^{-1} were recorded on a Perkin-Elmer 683 spectrophotometer using KBr as a dilution matrix, FIR spectra (400–80 cm^{-1}) on a Bruker IFl13v instrument in a polyethylene matrix, and ^{1}H NMR

Table 3 Crystallographic data and experimental details for complexes **1** and **2**

	1	**2**
Formula	$C_{50}H_{50}N_4O_{12}Zn_3$	$C_{51}H_{81}Cl_3N_6O_{27}Zn_6$
M	1095.10	1708.87
Crystal system	Monoclinic	Trigonal (hexagonal setting)
Space group	$P2_1/c$	$R\bar{3}c$
a/Å	10.389(2)	20.975(7)
b/Å	9.807(2)	
c/Å	22.326(5)	26.049(7)
β/°	90.80(2)	
U/Å^3	2274	9925
2θ Range/°	4–54	5–54
Lattice segment	$+h, +k, \pm l$	$+h, +k, \pm l; h > l$
Z	2	6
D_c/g cm^{-3}	1.599	1.792
Crystal size/mm	0.48 × 0.45 × 0.20	0.15 × 0.08 × 0.17
Crystal shape and colour	Light yellow rhombus	Colourless rhombus
μ/mm^{-1}	1.64	2.35
Maximum, minimum transmission factors	0.470, 0.163	0.649, 0.399
Unique data	5334	4786
Observed data [$I > 2\sigma(I)$]	3865	1285[a]
Number of parameters	337	164
Maximum, minimum Δρ/e Å^{-3}	0.82, −0.81	0.44, −0.41
$R1$ [$I > 2\sigma(I)$], $wR2$ (all data)[b]	0.0344, 0.0330	0.0370, 0.0337
Goodness of fit	1.0693	0.6648

[a] The small number of reflections with $I > 2\sigma(I)$ is caused by the small crystal size. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w^{-1} = \sigma^2(F_o) + 0.0001F_o$.

spectra on a Bruker WH300 instrument with chemical shifts reported in parts per million (ppm) relative to an internal standard of tetramethylsilane. All chemical analyses were performed at the Institute of Organic Chemistry, University of Münster.

Synthesis

1,3-Bis(salicylidenamino)propan-2-ol[10a] (H_2hsalpn) and 4-methyl-2,6-bis(morpholinomethyl)phenol[26] (Hbmmp) were prepared according to literature methods.

[Zn$_3$(O$_2$CPh)$_2$(hsalpn)$_2$]·2MeOH 1. The salt $Zn(ClO_4)_2 \cdot 6H_2O$ (250 mg, 0.67 mmol) was dissolved in methanol (6 cm^3) and added to a solution of H_2hsalpn (200 mg, 0.67 mmol) in methanol (10 cm^3). After addition of sodium benzoate (100 mg, 0.67 mmol) in methanol (6 cm^3) the reaction mixture was filtered. After a few days yellow crystals were filtered off and washed with methanol. Yield 200 mg, 27% (Found: C, 54.25; H, 4.20; N, 5.05. $C_{50}H_{50}N_4O_{12}Zn_3$ requires C, 54.85; H, 4.60; N, 5.10%). δ_H(CD$_3$CN) 3.17 (4 H, d), 4.10 (1 H, t), 5.35 (1 H, s), 6.38 (2 H, d), 6.63 (2 H, m), 6.90 (2 H, m), 7.15 (2 H, d), 7.35 (2 H, m), 7.73 (1 H, m), 7.94 (2 H, d) and 8.26 (2 H, s).

[Zn$_6$(OH)$_6$(bmmp)$_3$][ClO$_4$]$_3$ 2. A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (480 mg, 1.30 mmol) in ethanol (25 cm^3) is added to a solution of Hbmmp (200 mg, 0.65 mmol) in methanol (25 cm^3). Slow evaporation of the solvent mixture resulted in colourless crystals which were filtered off. Yield 200 mg, 18% (Found: C, 36.15; H, 4.95; N, 4.85. $C_{51}H_{81}Cl_3N_6O_{27}Zn_6$ requires C, 35.85; H, 4.80; N, 4.90%). δ_H(dimethylsulfoxide-d$_6$) 2.15 (3 H, s), 2.40 (8 H, t), 3.50 (4 H, s), 3.56 (8 H, t) and 6.83 (2 H, s).

Crystallography

Crystal data and data collection and refinement parameters for compounds **1** and **2** are given in Table 3.

Data collection and processing. Intensity data were collected at 150 K on a Syntex P2$_1$ (**1**) and on a Siemens P3 (**2**) diffractometer (Mo-Kα radiation, λ = 0.710 73 Å, graphite monochromator) by using ω–2θ scans and a variable scan rate (2–29° min^{-1}). The intensities of two reflections were monitored and no significant crystal deterioration was observed. Data were corrected for Lorentz-polarization factors and empirically for absorption (ψ scans).[27]

Structure solution and refinement. The structures were solved by direct methods.[27] A series of full-matrix least-squares refinement cycles on F followed by Fourier syntheses gave all remaining atoms. The hydrogen atoms H(1), H(3) and H(11) of the ligand hsalpn^{2-} in **1** and the three hydrogen atoms of the methyl group of the methanol solvent molecule were located in the Fourier-difference map and refined with isotropic thermal parameters, as well as H(3) the hydrogen atom belonging to the hydroxy groups in **2**. All other hydrogen atoms in both structures were calculated and allowed to ride on their corresponding carbon atoms. The isotropic thermal parameters for the calculated hydrogen atoms in **1** were 1.3 times the U_{eq} value of the bonding atom. The isotropic thermal parameters for the calculated hydrogen atoms in **2** were refined in groups: $U_H(CH_3) = 0.020(15)$, $U_H(CH_2) = 0.036(4)$ and $U_H(CH_{arom}) = 0.056(18)$ Å^2. All non-hydrogen atoms of complexes **1** and **2** were refined anisotropically. Owing to the fact that the atoms Cl(1) and O(4) of the perchlorate group in **2** are located on a two-fold axis, the other oxygen atoms of the anion are disordered in two positions. As a result O(5)–O(7) were refined with occupancy factors of 0.5. The atoms O(1), C(1), C(4) and C(5) in **2** are positioned on a two-fold axis and Zn(2) in **1** is located on a crystallographic inversion centre.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/179.

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