

Dinuclear Zinc(II) Complexes of *N,N'*-Bis[2-(hydroxyphenyl)methyl]-*N,N'*-bis(2-pyridylmethyl)-1,*n*-alkanediamines

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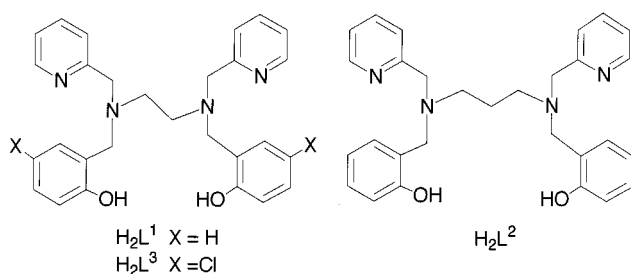
Keywords: Zinc / N ligands / O ligands / Structure elucidation

Neutral homodinuclear zinc(II) complexes $[\text{ZnL}]\cdot\text{ZnCl}_2$ have been obtained from the reactions of the proligands *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)-1,2-ethanediamine (H_2L^1) and *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)-1,3-propanediamine (H_2L^2) with zinc chloride. Crystals of $[\text{ZnL}^1]\cdot\text{ZnCl}_2$ (**3**) are triclinic, of space group $P1(\text{bar})$, with $a = 9.2240(7)$, $b = 10.4005(9)$, and $c = 15.6418(13)$ Å, $\alpha = 91.634(2)$, $\beta = 91.566(2)$, $\gamma = 112.625(2)^\circ$ and $Z = 2$, and those of $[\text{ZnL}^2]\cdot\text{ZnCl}_2$ (**2**) are monoclinic, of space group $P2_1/c$, with $a = 19.249(4)$, $b = 17.275(4)$, and $c = 16.546(3)$ Å, $\beta = 92.742(5)^\circ$ and $Z = 8$. The structures were refined by full-matrix least-squares procedures to $R_1 = 0.0589$

for **3** and $R_1 = 0.085$ for **2** for 4080 and 3786 independent reflections with $I \geq 4\sigma(I)$ respectively. The Zn in the $[\text{ZnL}]$ moiety is coordinated in a distorted octahedral geometry $[\text{N}_2\text{N}'_2\text{O}_2]$ and this unit serves as a chelating ligand, through the pair of phenolic O atoms, towards the ZnCl_2 . The second zinc atom is in a distorted tetrahedral geometry. The structure of **2** shows a racemic mixture of two enantiomers, in which the pendant pyridinyl N atoms are *trans* to each other, whereas the structure of **3** reveals a new stereoisomer in which the pendant pyridinyl N atoms are *cis* to each. ^1H NMR spectroscopic data for the complexes shows a rigid solution structure for **2** and fluxional behaviour for **3**.

Introduction

An interest in generating models for manganese-containing metallobiosites led Neves et al. to synthesise mononuclear manganese(III) complexes of the *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)-1,*n*-alkanediamine ligands H_2L^1 ($n = 2$) and H_2L^2 ($n = 3$).^[1] The crystal structure of $[\text{MnL}^1]\text{PF}_6$ revealed that the manganese(III) is present in a pseudo-octahedral geometry with each of the two halves of the hexadentate ligand providing a facial N_2O donor set. The phenolic O-atoms were found to be *cis* to each other and, with the N-atoms of the ethylenic spacer, provided the equatorial donor array.



The pyridinyl N-atoms are in the apical sites and so are *trans* to each other. Similar pseudo-octahedral geometries and ligand dispositions have been found for gallium(III) and indium(III) in the closely related mononuclear complexes $[\text{ML}^3]\text{ClO}_4$ ($\text{M} = \text{Ga}, \text{In}$),^[2] and for vanadium(III) in the complex $[\text{VL}^1]\text{PF}_6$.^[3] The hexadentate ligands

$[\text{O}^-(\text{N}^-\text{N}_{\text{pyr}})^-(\text{N}^-\text{N}_{\text{pyr}})^-\text{O}]$ have the capability to produce stereoisomers (Figure 1) but only (**1a**) has been crystallographically characterised in the above-mentioned complexes.

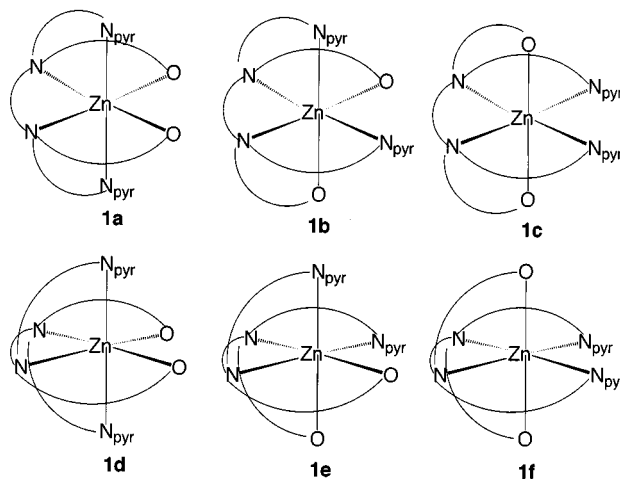
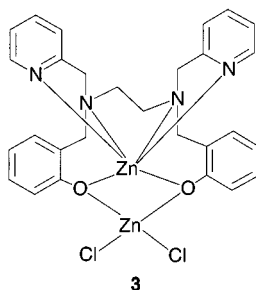
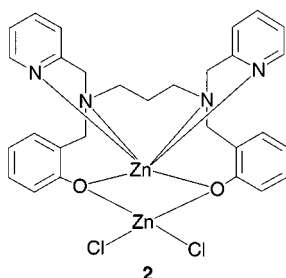


Figure 1. Octahedral stereoisomers derived from the ligands $[\text{O}^-(\text{N}^-\text{N}_{\text{pyr}})^-(\text{N}^-\text{N}_{\text{pyr}})^-\text{O}]$

During the course of an investigation into the complexation of zinc(II) by tripodal and linked polypodal ligands bearing phenolic and pyridinyl groups^[4–6] we have found that, in contrast to the above generation of mononuclear trivalent metal complexes, the reaction of zinc(II) chloride with H_2L^2 and H_2L^1 gives the homodinuclear complexes **2** and **3**, respectively, in which the anticipated neutral hexadentate zinc(II) complexes are not isolated but act as ligands towards a zinc chloride entity. In this paper we report this reactivity together with the crystal structures of

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the resulting complexes. Prior to this report, studies of H_2L^1 and H_2L^2 with divalent metals have been restricted to those on the application of H_2L^1 in the extraction of divalent first row transition metals into $CHCl_3$ in which the speciation revealed that the ligand could act not only in a hexadentate mode but also in tri- and tetradentate modes to give positively charged species.^[7]



Results and Discussion

The Complex $[ZnL^2] \cdot ZnCl_2$ (2)

Reaction of the ligand H_2L^2 with two equivalents of $ZnCl_2$ in acetonitrile solution in the presence of NEt_3 gave colourless crystals suitable for X-ray analysis. The analytical data suggested that a complex with a molecular formula $[Zn_2L^2Cl_2]$ had formed and it was noted that changing the ratio of the starting materials from 1:2 to 1:1 did not change the stoichiometry of the reaction product. As a dinuclear product had not been expected the crystal structure was determined in order to establish the bond connectivity. There are two enantiomeric molecules in the asymmetric unit. The molecular structure of each, depicted in Figure 2, revealed that one Zn atom is completely encapsulated by the deprotonated ligand in a pseudo-octahedral coordination environment similar to that found in $[MnL^1]PF_6$, and in contrast to the structure found for $Zn(L^4)_2 \cdot 2H_2O$, in which there is no steric constraint imposed by an alkane linker joining the secondary amines and the phenolate-O atoms are *trans* to each other, as are the pyridinyl-N atoms.^[8] This octahedral complex $[ZnL^2]$ acts as a ligand with the *cis*-phenolate O-atoms chelating to the second zinc atom to give the product $[ZnL^2] \cdot ZnCl_2$ (2).

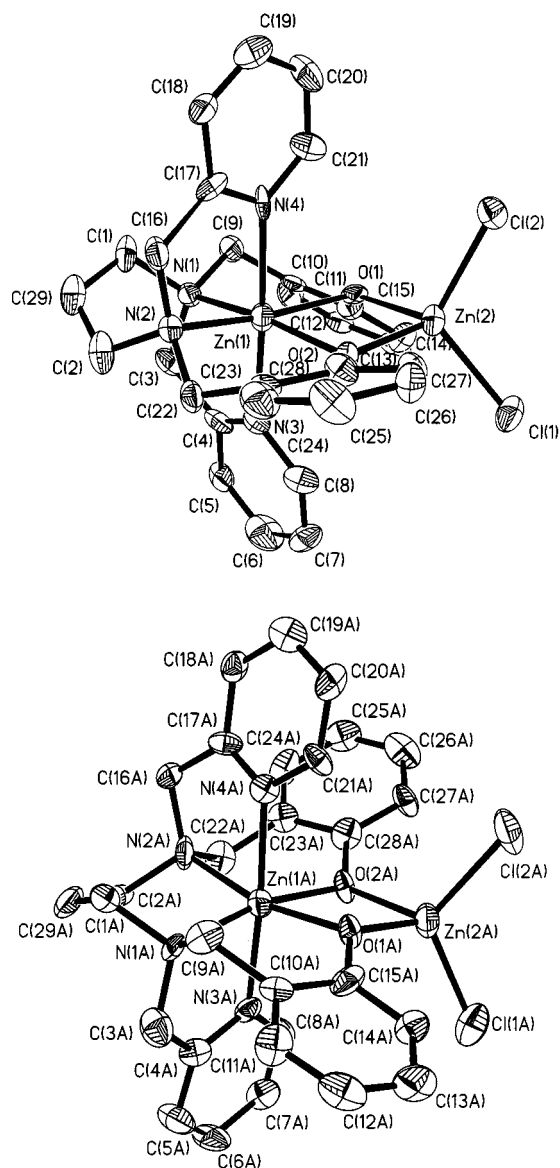
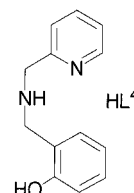
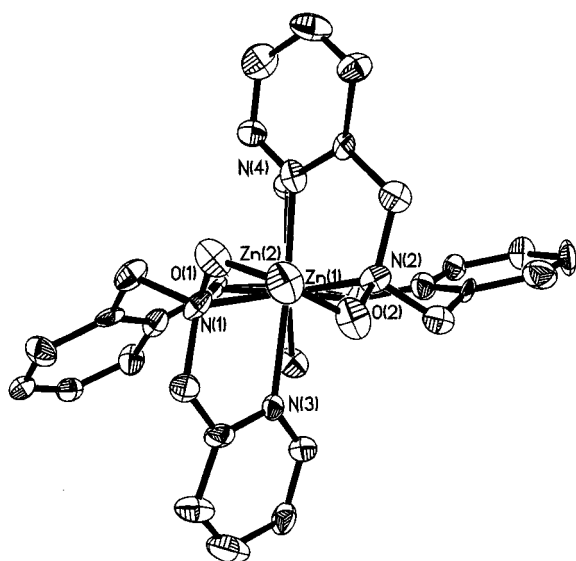


Figure 2. ORTEP drawings of the enantiomers of $[ZnL^2] \cdot ZnCl_2$ [Δ -2 (a) and Λ -2 (b)] showing the crystallographic labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level

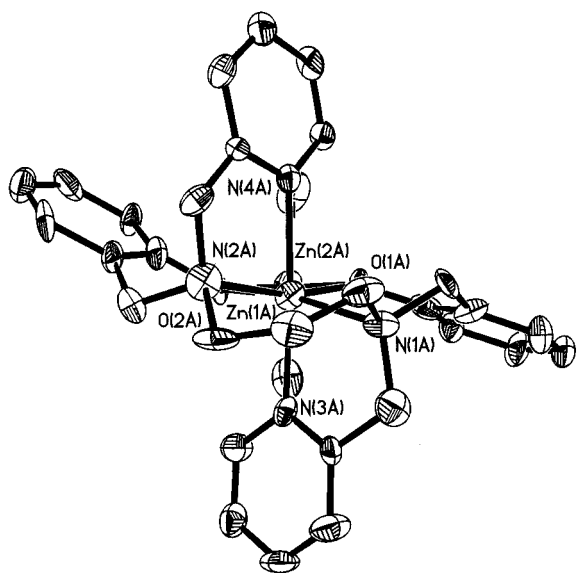


The reaction of H_2L^2 with zinc(II) acetate yields the related complex $[ZnL^2] \cdot Zn(OAc)_2$ in which the octahedral $[ZnL^2]$ unit, derived from stereoisomer **1a**, coordinates to the $Zn(OAc)_2$ through the *cis*-phenolato O atoms. The two acetato groups are monodentate and the second Zn atom is in a distorted T_d environment.^[9]

The second zinc atom has a distorted tetrahedral coordination environment with two Cl atoms completing the coordination sphere. The Δ enantiomer (**1d**) is that containing Zn(1) and Zn(2), and the Λ enantiomer (**1a**) is that containing Zn(1A) and Zn(2A) (Figure 3); the designations Λ and Δ have been assigned assuming the species are trischelates with atom sequences O(1)Zn(2)O(2),



a.



b.

Figure 3. ORTEP drawings of the enantiomers of $[\text{ZnL}_2] \cdot \text{ZnCl}_2$ [Δ -**2** (a) and Λ -**2** (b)] viewed along the equatorial plane $[\text{N}(1) - \text{N}(2) - \text{O}(1) - \text{O}(2)]$; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level

$\text{N}(2)\text{C}(16)\text{C}(17)\text{N}(4)$, and $\text{N}(1)\text{C}(3)\text{C}(4)\text{N}(3)$ serving as chelating ligands.

Bond lengths and angles relating to the coordination at the metals are given in Table 1. The three *trans* angles in the octahedral sector of the Δ enantiomer, $\text{N}(3) - \text{Zn}(1) - \text{N}(4)$, $\text{N}(1) - \text{Zn}(1) - \text{O}(2)$, and $\text{N}(2) - \text{Zn}(1) - \text{O}(1)$ are $175.2(3)$, $168.6(3)$, and $169.2(3)^\circ$ respectively, and those in the Λ enantiomer, $\text{N}(4\text{A}) - \text{Zn}(1\text{A}) - \text{N}(3\text{A})$, $\text{N}(1\text{A}) - \text{Zn}(1\text{A}) - \text{O}(2\text{A})$, and $\text{N}(2\text{A}) - \text{Zn}(1\text{A}) - \text{O}(1\text{A})$ are $174.8(3)$, $167.6(3)$, and $167.1(3)^\circ$ respectively, indicating some distortion from a pure octahedral geometry. The Zn–O bond lengths for Zn–phenolate interactions average 2.08 \AA and are shorter than those for the Zn–amine interactions (average length = 2.17 \AA) and those for the Zn–pyridyl interactions (average length = 2.14 \AA).

Table 1. Selected bond lengths [\AA] and bond angles [$^\circ$] for complexes **2** and **3**

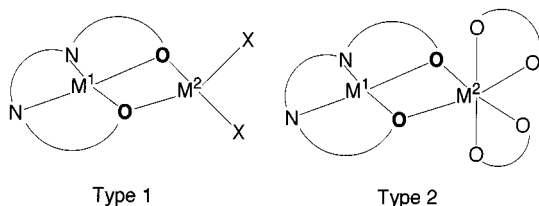
	Δ - 2	Λ - 2 ^[a]	3
Zn(1)–O(1)	2.101(6)	2.083(6)	2.084(3)
Zn(1)–O(2)	2.070(6)	2.059(6)	2.172(3)
Zn(1)–N(1)	2.176(7)	2.177(8)	2.181(4)
Zn(1)–N(2)	2.155(8)	2.162(8)	2.200(4)
Zn(1)–N(3)	2.133(8)	2.127(8)	2.169(4)
Zn(1)–N(4)	2.156(8)	2.136(8)	2.122(4)
Zn(1)–Zn(2)	3.0540(18)	3.0474(18)	3.1171(8)
Zn(2)–O(1)	1.997(6)	1.979(6)	1.992(3)
Zn(2)–O(2)	1.997(6)	1.998(6)	1.969(3)
Zn(2)–Cl(1)	2.224(3)	2.221(3)	2.2163(14)
Zn(2)–Cl(2)	2.231(3)	2.233(3)	2.2483(13)
N(1)–Zn(1)–O(2)	168.6(3)	167.6(3)	109.18(13)
N(2)–Zn(1)–O(1)	169.2(3)	167.1(3)	160.50(14)
N(3)–Zn(1)–N(4)	175.2(3)	174.8(3)	90.47(15)
N(2)–Zn(1)–N(1)	94.2(3)	94.9(3)	81.93(15)
N(2)–Zn(1)–O(2)	93.4(3)	93.5(3)	87.11(14)
N(1)–Zn(1)–O(1)	93.1(3)	93.0(3)	91.67(14)
O(1)–Zn(1)–O(2)	80.6(2)	80.5(2)	77.57(12)
N(3)–Zn(1)–N(2)	100.9(3)	96.9(3)	108.72(15)
N(3)–Zn(1)–N(1)	78.8(3)	80.1(3)	78.43(14)
N(3)–Zn(1)–O(2)	91.4(3)	89.8(3)	163.52(13)
N(3)–Zn(1)–O(1)	88.3(3)	94.4(3)	87.79(14)
N(4)–Zn(1)–N(2)	79.7(3)	77.9(3)	79.53(15)
N(4)–Zn(1)–N(1)	96.4(3)	99.5(3)	154.04(15)
N(4)–Zn(1)–O(2)	93.3(3)	91.2(3)	87.92(14)
N(4)–Zn(1)–O(1)	91.6(3)	90.8(3)	111.49(14)
O(2)–Zn(2)–O(1)	85.0(2)	84.6(3)	84.63(13)
Cl(1)–Zn(2)–Cl(2)	113.98(13)	117.22(13)	116.63(5)
O(2)–Zn(2)–Cl(1)	110.9(2)	113.2(2)	111.99(10)
O(2)–Zn(2)–Cl(2)	115.12(19)	115.1(2)	116.92(10)
O(1)–Zn(2)–Cl(1)	119.88(19)	114.0(2)	115.79(10)
O(1)–Zn(2)–Cl(2)	108.90(19)	108.1(2)	106.66(10)
Zn(1)–O(1)–Zn(2)	96.3(3)	97.2(3)	99.72(14)
Zn(1)–O(2)–Zn(2)	97.3(2)	97.4(3)	97.54(14)

^[a] The atomic labelling sequence for Λ -**2** in Figures 2 and 3 is 1A, 2A, 3A etc. corresponding directly to that for Δ -**2** of 1, 2, 3 etc.

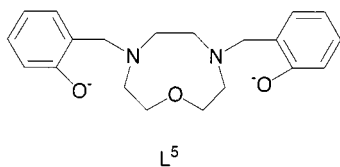
The coordination environment of the second zinc atom in each enantiomer is a distorted tetrahedron. The bond angles for the chelated O–Zn–O are $85.0(2)^\circ$ $[\text{O}(1) - \text{Zn}(2) - \text{O}(2)]$ and $84.6(3)^\circ$ $[\text{O}(1\text{A}) - \text{Zn}(2\text{A}) - \text{O}(2\text{A})]$, and $113.98(11)^\circ$ and $117.22(13)^\circ$ for the Cl–Zn–Cl angles $\text{Cl}(1) - \text{Zn}(2) - \text{Cl}(2)$ and $\text{Cl}(1\text{A}) - \text{Zn}(2\text{A}) - \text{Cl}(2\text{A})$ respectively. The remaining O–Zn–Cl angles are closer to the expected tetrahedral values. The Zn–O bonds (average length = 1.99 \AA) are shorter than those at Zn(1) and Zn(1A) and the Zn–Cl bond lengths average 2.23 \AA . The

intermetallic separations are 3.0540(18) [Zn(1)⋯Zn(2)] and 3.0474(18) Å [Zn(1A)⋯Zn(2A)].

Although the role of transition metal complexes as ligands has been well established for complexes of tetradentate salicylaldimines such as salen (salen = *N,N'*-ethylenebis(salicylideneimine)[2,2'-{1,2-ethanediylbis(nitrilomethylidene)phenol}])^[10] the above complex is a novel example of a hexadentate metal complex acting as a donor ligand towards a second metal atom. Previously, dinuclear zinc(II) complexes of the type Zn(TSB)ZnX₂ (X = Cl, ClO₄; TSB = tetradentate Schiff base), in which both zinc atoms were regarded as four-coordinate with a square coplanar Zn atom from the Schiff base adjacent to a tetrahedral Zn atom in the inorganic salt (Type 1), have been reported but no X-ray structural characterisation was made.^[11,12] Homo- and heterodinuclear complexes in which a square coplanar Schiff base complex acts as a bidentate ligand towards a coordinatively unsaturated bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)metal(II) (Type 2) have also been reported.^[13–18]



In contrast the current compounds have a six-coordinated metal complex acting as a ligand towards an inorganic salt and resemble the coordination pattern found in the complex [L⁵Zn(OH₂)ZnCl₂]·0.5 CH₃CN.^[19] In this compound one of the zinc atoms is octahedrally coordinated by the pentadentate dianionic macrocyclic ligand (L⁵) and a water molecule, whilst the second zinc atom is tetrahedrally coordinated to two bridging phenolate oxygen atoms and to two chloride ions. The Zn⋯Zn separation was given as 3.08 Å but further details on bonds and angles were not released as the poor crystallinity of the crystals inhibited an accurate structure determination.



The Complex [ZnL¹]⁺·ZnCl₂[−] (3)

The reaction of ZnCl₂ with H₂L¹ gave the complex [ZnL¹]⁺·ZnCl₂[−] (3). Intriguingly the crystal structure revealed that a different spatial arrangement of donor atoms was present (Figure 4). Instead of the pyridine N-atoms being *trans* to each other they are now *cis* [N(3)–Zn(1)–N(4),

90.47(15)°, **1b**] and so give rise to a previously unreported stereoisomer for this class of compounds. There are two molecules, an enantiomeric pair, in the triclinic unit cell, with only one molecule in the asymmetric unit; the opposite enantiomer is generated by the inversion centre of the *P*1(*bar*) space group.

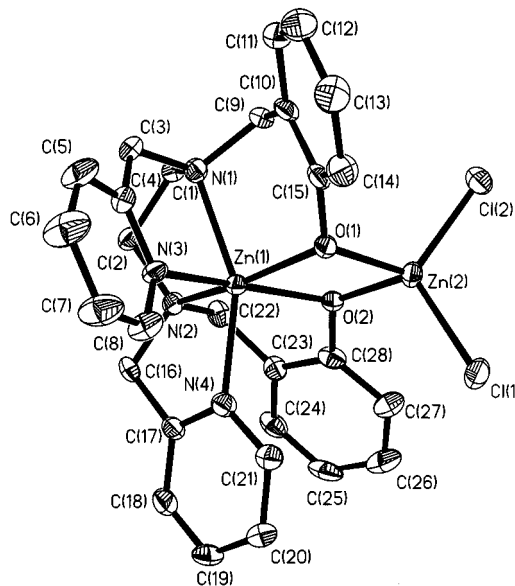


Figure 4. ORTEP drawing of [ZnL¹]⁺·ZnCl₂[−] (3) showing the crystallographic labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level

Bond lengths and angles relating to the coordination at the metals are given in Table 1. The three *trans* angles in the octahedral sector of the molecule, N(1)–Zn(1)–N(4), N(3)–Zn(1)–O(2), and N(2)–Zn(1)–O(1) are 154.04(15), 163.52(13), and 160.50(14)°, respectively, and are indicative of a larger distortion of the octahedral coordination geometry at Zn(1). The Zn–O bond lengths for Zn–phenolate interactions are 2.084(3) [Zn(1)–O(1)] and 2.172(3) Å [Zn(1)–O(2)], and are again shorter than those for the Zn–amine interactions, 2.181(4) [Zn(1)–N(1)] and 2.200(4) Å [Zn(1)–N(2)], and those for the Zn–pyridyl interactions of 2.169(4) [Zn(1)–N(3)] and 2.122(4) Å [Zn(1)–N(4)]. The five-membered ring (ZnNC₂N) formed by the ethylenediamine linker has a skew conformation with a torsion angle N(1)–C(1)–C(2)–N(2) of −59.4° and the two carbon atoms of the linker, C(1) and C(2), are displaced by 0.43 and −0.30 Å on opposite sides of the ZnNN plane.

The second zinc atom is again in a tetrahedrally distorted coordination environment. The bond angle for the chelated O–Zn–O is 84.63(13)° [O(1)–Zn(2)–O(2)] and 113.63(5)° for the Cl–Zn–Cl angle [Cl(1)–Zn(2)–Cl(2)]. The remaining O–Zn–Cl angles are slightly more divergent [106.66(10)–116.92(10)°] from the expected tetrahedral values than in **2**. The Zn–O bonds (average length = 1.98 Å) are shorter than those at Zn(1) and the Zn–Cl bond lengths average 2.23 Å introducing further asymmetry to the tetrahedral site. The intermetallic separation of 3.1171(8) Å [Zn(1)⋯Zn(2)] is longer than that found in **2**.

Solution Studies

The ^1H NMR spectra of the metal complexes were recorded in $[\text{D}_6]\text{DMSO}$. The spectrum of **2** was sharp, as had been noted for the spectra of the closely related mononuclear gallium(III) and indium(III) complexes $[\text{ML}]\text{ClO}_4$ ($\text{L} = \text{L}^1, \text{L}^3$).^[2] The spectra of these complexes did not undergo significant changes on raising the temperature from room temperature to 120 °C, indicating the intact and rigid nature of the octahedral complexes in solution. The structure is possibly stabilised by the presence of six-membered chelate rings, formed by the phenolic arms, in their preferred equatorial configuration.^[1,20] The minor shifts of the ^1H resonance signals and slight broadenings of the signals were attributed to thermal vibrations of the coordinated ligands at elevated temperatures.^[2] In contrast, although the resonances of **3** are close in value to those reported for the corresponding gallium and indium complexes some of them showed significant broadening at room temperature. An enhancement of the broadening and changes in chemical shifts occurred as the temperature was raised to 100 °C. This suggests that there are dynamic processes occurring over this temperature range. It was not possible to freeze any molecular motions due to the solution range of $[\text{D}_6]\text{DMSO}$, nor was it possible to obtain a limiting high temperature spectrum. It is proposed that the stereoisomer found in the solid state (**1b**), in which one of the six-membered chelate rings formed by the phenolic arms is in an equatorial configuration and the other is in an axial configuration, is less rigid than the stereoisomer **1a** in which both six-membered chelate rings formed by the phenolic arms are equatorial. Interconversion of the arms together with accompanying movement of the ethane linker would lead to the resonance broadening that is observed.

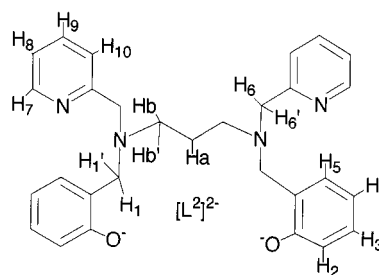
Conclusions

In contrast to the reactions of H_2L^1 and H_2L^2 with trivalent metals, which gave discrete mononuclear complex cations, zinc chloride reacts with H_2L^2 and H_2L^1 to give the dinuclear zinc(II) complexes **2** and **3**. In these complexes one zinc(II) atom is fully encapsulated by the deprotonated hexadentate ligand in a pseudo-octahedral geometry and this moiety then acts as a ligand towards ZnCl_2 through the *cis*-phenolato-O atoms. The second zinc(II) atom is in a distorted tetrahedral coordination environment. The structure of **2**, in which the pyridinyl N donors are *trans* to each other, is similar to those found for the trivalent metal complexes of L^1 in which the stereoisomer **1a** is found, but the structure of **2** further showed the presence in the asymmetric unit of a racemic mixture of the two enantiomers Λ (**1a**) and Δ (**1d**). The structure of **3** revealed a previously unreported second stereoisomer **1b** in which the pyridinyl N donors are *cis* to each other; in this case only one enantiomer was present in the asymmetric unit with the opposite enantiomer being generated from an inversion centre [$P\bar{1}$ space group].

Experimental Section

Measurements: Elemental analyses were carried out by the University of Sheffield microanalytical service. ^1H NMR spectra were recorded using a Bruker WH-400 spectrometer. Positive ion fast atom bombardment (FAB) mass spectra were recorded using a VG PRO-SPEC spectrometer (the matrix used was 4-nitrobenzyl alcohol).

Materials: Reagent or AR grade chemicals were used in this study. N,N' -bis(2-hydroxybenzyl)- N,N' -bis(2-methylpyridyl)-1,2-ethanediamine (H_2L^1) and the N,N' -bis(2-hydroxybenzyl)- N,N' -bis(2-methylpyridyl)-1,3-propanediamine (H_2L^2) were prepared by the published methods.^[1,2]



Synthesis of Complexes

$[\text{Zn}(\text{L}^2)\cdot\text{ZnCl}_2]$ (2**):** N,N' -bis(2-hydroxybenzyl)- N,N' -bis(2-methylpyridyl)-1,3-propanediamine (100 mg, 0.21 mmol) was dissolved in warm acetonitrile (10 mL) containing a trace amount of NEt_3 . ZnCl_2 (60 mg; 0.44 mmol) was added and the solution was gently refluxed for 1 hour. After cooling and standing the solution afforded colourless crystals suitable for X-ray analysis. Yield: 84 mg, 60%. – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 8.85 (d, 2 H, 7-H), 7.71 (t, 2 H, 8-H), 7.27 (t, 2 H, 9-H), 7.04 (d, 2 H, 10-H), 6.95 (d, 2 H, 5-H), 6.81 (t, 2 H, 4-H), 6.64 (d, 2 H, 2-H), 6.45 (t, 2 H, 3-H), 4.33 (d, 2 H, 6'-H), 4.15 (d, 2 H, 1'-H), 3.73 (d, 2 H, 6-H), 3.36 (d, 2 H, 1-H), 2.79 (m, 2 H, b'-H), 2.64 (m, 2 H, b-H), 2.21 (bd, 2H, a-H). – MS (FAB; $m\text{NBA}$): m/z = 531 $[\text{Zn}(\text{L}^2) + \text{H}]^+$. – $\text{C}_{29}\text{H}_{30}\text{Cl}_2\text{N}_4\text{O}_2\text{Zn}_2$ (668.2): calcd. C 52.12, H 4.52, N 8.38, Cl 10.61; found C 52.03, H 4.56, N 8.23, Cl 10.90.

Table 2. Crystallographic data for **2** and **3**

	2	3
Formula	$\text{C}_{29}\text{H}_{30}\text{Cl}_2\text{N}_4\text{O}_2\text{Zn}_2$	$\text{C}_{28}\text{H}_{28}\text{Cl}_2\text{N}_4\text{O}_2\text{Zn}_2$
Formula mass	668.21	654.18
Space group, Z	$P2_1/c$, 8	$P\bar{1}$, 2
Wavelength [Å]	0.71073	0.71073
a [Å]	19.249(4)	9.2240(7)
b [Å]	17.275(4)	10.4005(9)
c [Å]	16.546(3)	15.6418(13)
α [deg]	90	91.634(2)
β [deg]	92.742(5)	91.566(2)
γ [deg]	90	112.625(2)
V [Å ³]	5496(5)	1386.3(2)
T [K]	150(2)	150(2)
ρ_{calc} [mg·m ⁻³]	1.615	1.567
μ [mm ⁻¹]	1.976	1.956
Final R ^[a]	$R_1 = 0.085$ $wR_2 = 0.1604$	$R_1 = 0.0589$ $wR_2 = 0.1256$

^[a] $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ with $I > 4\sigma(I)$ and $wR_2 = \frac{\{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]\}^{1/2}}$.

[Zn(L¹):ZnCl₂] (3): *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)-1,2-ethanediamine (100 mg; 0.22 mmol) was dissolved in warm acetonitrile (8 mL) containing a trace amount of NEt₃ and ZnCl₂ (60 mg; 0.44 mmol) was added. The solution was gently refluxed for 1 hour. After cooling and standing the solution gave colourless crystals suitable for X-ray analysis. Yield, 107 mg; 74.6%. – ¹H NMR ([D₆]DMSO); aromatics at δ = 8.80 (d), 7.75 (bd), 7.32 (t), 7.06 (bd), 6.98 (d), 6.77 (t), 6.42 (t), 6.15 (bd); aliphatics at δ = 4.25 (bd), 4.08 (d), 3.96 (bd), 3.55 (d), 3.05 (bd), 2.70 (bd). – MS (FAB; *m*NBA): *m/z* = 517 [Zn(L¹) + H]⁺. – C₂₈H₂₈Cl₂N₄O₂Zn₂ (654.2): calcd. C 51.41, H 4.31, N 8.56, Cl 10.84; found C 51.48, H 4.28, N 8.37, Cl 10.92.

X-ray Crystallography: Relevant X-ray crystal data are given in Table 2. Measurements were made on a Siemens SMART CCD area diffractometer using graphite-monochromatised Mo-*K*_α radiation, λ = 0.71073 Å. The programs used were Siemens SMART and SAINT for control and integration software and SHELXTL as implemented on the Viglen Pentium computer.^[21]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication nos. CCDC-148463 (2) and -148464 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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