Zinc(II) coordination polymers with pseudopeptidic ligands

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13 **Abstract**

14 Two new phenyl-bridged pseudopeptidic ligands have been prepared and structurally
15 characterised. The nature of the ligands' substituents seem to play an important role in the
16 nature of the solid state structure yielding either hydrogen bonded linked sheets of molecules
17 or infinite hydrogen bonded networks. Both these ligands were reacted with a range of
18 zinc(II) salts with the aim of synthesising coordination polymers and networks and explore
19 the role that anions could play in determining the final structure. The crystal structures of four
20 of these systems (with ZnSO_4 and ZnBr_2) were determined; in one case, a 3D coordination
21 network was obtained where zinc-ligand coordination bonds generated the 3D arrangements.
22 Three other 3D networks were obtained by anion-mediated hydrogen bonding of coordination
23 1D chains or 2D sheets. These four very different structures highlight the important role
24 played by the ligands' substituents and the counteranions present in the system.

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Introduction

Coordination of metal cations by proteins and peptidic fragments is, very often, an essential factor for many biochemical events. Thus, it is not surprising that many efforts have been devoted to developing different catalytic systems based on the coordination of pseudo-peptidic ligands to different metals.¹⁻⁴ In this regard, we have recently studied the Cu^{2+} and Zn^{2+} coordination properties of simple C_2 symmetric pseudo-peptides such as **1** (see Scheme 1) in which two valine fragments are connected by an aliphatic spacer $(-\text{CH}_2)_n$.⁵⁻¹² Spectroscopic, mass spectrometric and X-ray crystallographic studies, revealed that the corresponding complexes can adopt a variety of coordination geometries depending on several factors such as nature of the cation, pH of the medium and the length of the central aliphatic spacer. Of particular relevance was the observation that, by varying these factors, complexes of different stoichiometries could be obtained. This is schematically presented in Scheme 1 showing the possibility of obtaining in these systems, discrete complexes with 1:1 (A) and 2:2 (B) stoichiometries as well as coordination polymers (C).

Scheme 1. Possible stoichiometries for coordination complexes with pseudo-peptidic ligands.

In our previous studies with receptors type **1** with flexible central spacers, it was also observed that the nature of this spacer, is key for determining the structure of the complex formed. Thus, it is reasonable to assume that introduction of a rigid aromatic spacer in the pseudopeptidic ligand could provide a tool for better defining the structure of the resulting metal complexes.¹³⁻¹⁵ Taking this into consideration it was rationalised that the substitution of the polymethylene fragment by para-phenylene using 1,4-diaminobenzene, could lead to the formation of new coordination polymers and networks. On the other hand, the preparation of derivatives from two different starting amino acids, namely valine and phenylalanine, was considered of interest in order to analyze and understand the role of the different side chains in determining both the structure and stability of the resulting metallo-assemblies. X-ray crystal structures from Phe derivatives of **1** (n=1) have previously revealed the formation of a nanoporous architecture containing π -channels through the association of the aromatic side chains via π - π interactions.¹⁶ In the case of some macrocyclic structures derived from **1**,^{6,17-22} the crystal structures of their HCl salts have allowed to highlight not only the importance of generic hydrophobic interaction for the assembling, but also the participation of specific structural factors including the so called “knobs into holes” complementarity.²³⁻²⁹

Coordination polymers based on amino acid backbones have recently gained widespread interest due to their intriguing properties³⁰⁻³² such as asymmetric catalysis, chiral sorption and varied coordination modes.³³

Herein we report the synthesis and structural characterisation of the two novel pseudopeptidic ligands **2** and **3** (see Scheme 2) and the resulting coordination networks from the reactions between these two ligands and different zinc(II) salts. We highlight the important role played by the ligands’ substituents in the final coordination networks obtained. On the other hand, since the templating role of anions in supramolecular³⁴⁻³⁷ and coordination chemistry³⁸⁻⁴²

(including the formation of coordination networks) is an area of considerable ongoing interest, we also aimed to establish whether anions would play an important role in the overall structure of the systems under study.

Results and Discussion

Synthesis and structural characterisation of pseudopeptidic ligands. Ligands **2** and **3** were prepared from enantiopure Cbz protected aminoacids following a synthetic protocol similar to the one used for the preparation of related pseudopeptides type **1**.⁴³ Because of the lower reactivity of 1,4-diaminobenzene than aliphatic diamines, ethyl chloroformate was used as the activating agent instead of *N*-hydroxysuccinimide. The Cbz protecting group was removed using a HBr/AcOH 33% mixture to yield pure ligands after neutralization with NaOH. The procedure is outlined in Scheme 2. The ligands were fully characterised by spectroscopic and analytic techniques (see Experimental Details), including circular dichroism (CD) spectroscopy which showed that bulk samples of the ligands are indeed chiral (see Supplementary Information).

Scheme 2. Reaction scheme for the preparation of ligands **2** and **3**.

Crystals of both ligands suitable for X-ray crystallography were obtained by slow evaporation of a solution of **2** in methanol and **3** in toluene. The structure of **2** was found to contain two crystallographically independent molecules, **2-A** and **2-B**, shown in Figs. 1 and S2 respectively. These are linked by eight intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds⁴⁴ to form phenyl-bound β -sheets – analogous to those observed in proteins; part of one of these sheets is shown in Fig. 2. It is interesting to note that despite the two amide substituents on the central aryl ring being the same, they have markedly different conformations in both independent molecules with $\{\text{N}(1)-\text{C}(2)-\text{C}(3)-\text{O}(3)\}$ and $\{\text{N}(14)-\text{C}(13)-\text{C}(12)-\text{O}(12)\}$ torsion angles of *ca.* 56 and 160° respectively in **2-A**, and *ca.* 55 and 163° respectively in **2-B**. This allows both of the hydrogen atoms of the N(1)-based NH_2 group to engage in hydrogen bonding (one intermolecular, and one intramolecular⁴⁵), whilst for the chemically equivalent N(14)-based NH_2 group the amide conformation precludes the equivalent intramolecular hydrogen bond and consequently one of the hydrogen atoms is not involved in any significant hydrogen bonding interaction.

Fig. 1 The molecular structure of one (**2-A**) of the two crystallographically independent molecules present in the structure of **2**.

Fig. 2 Part of one of the N–H...O hydrogen bonded linked sheets of molecules present in the structure of **2**, viewed along the *a* axis direction; molecule **2-A** has been drawn with dark bonds, and molecule **2-B** with open bonds.

The crystal structure of the isopropyl species **3** (Fig. 3) shows it to form an N–H...O linked⁴⁶ three-dimensional network in the solid state (Fig. 4) in contrast to its phenyl analogue **2**. This change in the packing motif is associated with a change in the conformation of the two amide units. For both independent molecules in **2**, the two amide units have noticeably different N–C–O torsion angles [*ca.* 56 and 162° for the N(1) and N(14)-based

units], whereas here in **3** both units have the approximately the same conformation with {N(1)–C(2)–C(3)–O(3)} and {N(14)–C(13)–C(12)–O(12)} torsion angles of *ca.* 171 and 144° respectively. These conformational differences relate to differing roles of the NH₂ groups. In **2**, for both independent molecules the N(1) and N(14) groups behave differently, with the former having both hydrogen atoms involved in N–H···O contacts (one intra- and one inter-molecular) and the latter having only the one hydrogen atom engaging in an intermolecular N–H···O hydrogen bond (the other not being involved in any significant hydrogen bonding interactions). Here in **3**, both NH₂ groups act like the N(14) groups in **2**, having one hydrogen atom involved in an intermolecular N–H···O hydrogen bond and one “unused”, with the result that there are no intramolecular hydrogen bonds.

Fig. 3 The molecular structure of **3**.

Fig. 4 Hydrogen bonding patterns (dotted line) in the structure of **3**: Illustration of the N-H...O hydrogen bonded linked sheets, viewed along the *b* axis direction(top); Part of the extended three-dimensional network of hydrogen bond network linked via NH₂ (blue) and oxygen (red) atoms, viewed along the *a* axis direction(bottom)..

Synthesis and structural characterisation of zinc(II) coordination networks. The reactions of both ligands **2** and **3** with several different zinc(II) salts were investigated (including X = sulphate, chloride, bromide and nitrate) but only in four cases was it possible to obtain single crystals suitable for X-ray crystallography. These were the crystalline products resulting from the reactions of ZnSO₄ and ZnBr₂ with both ligands **2** and **3** (see Scheme 2). The resulting coordination polymers were obtained by layering an ethanolic solution of the corresponding ligand onto an aqueous solution of the corresponding zinc(II)

salt. The metal-ligand stoichiometry and purity of the complexes was determined by elemental analyses, single crystal X-ray diffraction and thermogravimetric analyses (see below).

Scheme 2. Summary of coordination polymers **4-7** prepared and structurally characterised.

The structure of **4**, which features a 1:1 ratio between zinc and ligand **2**, was found to contain two crystallographically independent cationic chains, **4-A** and **4-B** (see Figs. 5, 6, S6 and S8) that propagate along the *a* and *b* axis directions respectively.

Fig. 5 The unique portion of one (**4-A**) of the two crystallographically independent cationic chains present in the structure of **4**.

Fig. 6 Part of one (**4-A**) of the two crystallographically independent cationic chains present in the structure of **4**.

Adjacent chains are held together by $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ hydrogen bonds involving the sulphate anions and solvent water molecules to form a three-dimensional network (Fig. 7).⁴⁷ The coordination of ligand **2** to a metal centre has an unsurprisingly marked effect on the conformation of the amide substituents with the $\{\text{N}(1)\text{--C}(2)\text{--C}(3)\text{--O}(3)\}$ and $\{\text{N}(14)\text{--C}(13)\text{--C}(12)\text{--O}(12)\}$ torsion angles being *ca.* 20 and 24° respectively in **4-A** (and *ca.* 27 and 24° respectively in **4-B**) *cf.* *ca.* 56 and 162° in **2**.

Fig. 7 Part of the extended 3D network of chains (linked via hydrogen bonds to the sulphate anions) present in the structure of **4**. The sulphate anions are shown in yellow, and the independent 1D coordination chains are shown in red (**4-A**) and blue (**4-B**).

Table 1. Selected bond lengths (Å) and angles (°) for both of the two crystallographically independent cationic chains (**4-A** and **4-B**) present in the structure of **4**.^[a]

	4-A	4-B		4-A	4-B
Zn(1)–N(1)	2.088(3)	2.114(3)	Zn(1)–O(3)	2.183(2)	2.174(3)
Zn(1)–O(29)	2.122(3)	2.111(3)	Zn(1)–O(30)	2.136(3)	2.102(3)
Zn(1)–O(12X)	2.173(2)	2.200(3)	Zn(1)–N(14X)	2.097(3)	2.127(3)
N(1)–Zn(1)–O(3)	77.82(10)	78.14(11)	N(1)–Zn(1)–O(29)	96.16(12)	92.44(12)
N(1)–Zn(1)–O(30)	94.27(11)	95.27(12)	N(1)–Zn(1)–O(12X)	95.87(10)	96.87(11)
N(1)–Zn(1)–N(14X)	169.47(11)	171.14(12)	O(3)–Zn(1)–O(29)	173.95(11)	170.56(11)
O(3)–Zn(1)–O(30)	92.63(11)	90.09(10)	O(3)–Zn(1)–O(12X)	93.23(10)	90.44(10)
O(3)–Zn(1)–N(14X)	93.84(11)	94.89(12)	O(29)–Zn(1)–O(30)	88.34(12)	91.55(11)
O(29)–Zn(1)–O(12X)	86.79(11)	89.94(10)	O(29)–Zn(1)–N(14X)	92.08(12)	94.40(13)
O(30)–Zn(1)–O(12X)	169.17(11)	167.70(11)	O(30)–Zn(1)–N(14X)	92.51(11)	90.17(12)
O(12X)–Zn(1)–N(14X)	78.02(10)	77.54(11)			

[a] The “X” suffix refers to the symmetry related atoms around the respective zinc centre. These are labelled with a “C” in Fig. 5 (showing molecule **4-A**), and with an “E” in Fig. S6 (showing molecule **4-B**).

The solid state structure of a crystal of **5** was found to contain a 1:1.5 ratio between zinc and ligand **2** *cf.* the 1:1 ratio seen in **4**. As such, the asymmetric unit of **5** contains one

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201 **Fig. 9** Part of the extended three-dimensional coordination network present in the structure
 202 of **5** (zinc atoms are shown in red; solvents and counteranions are omitted for
 203 clarity).
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205 **Table 2.** Selected bond lengths (Å) and angles (°) for **5**.

Zn(1)–N(1)	2.106(2)	Zn(1)–O(3)	2.1584(17)
Zn(1)–N(31)	2.152(2)	Zn(1)–O(33)	2.1340(17)
Zn(1)–O(12A)	2.2001(19)	Zn(1)–N(14A)	2.106(2)
N(1)–Zn(1)–O(3)	78.94(7)	N(1)–Zn(1)–N(31)	94.98(9)
N(1)–Zn(1)–O(33)	93.05(8)	N(1)–Zn(1)–O(12A)	87.92(8)
N(1)–Zn(1)–N(14A)	164.81(9)	O(3)–Zn(1)–N(31)	98.60(8)
O(3)–Zn(1)–O(33)	170.88(7)	O(3)–Zn(1)–O(12A)	93.19(7)
O(3)–Zn(1)–N(14A)	98.33(7)	N(31)–Zn(1)–O(33)	77.60(7)
N(31)–Zn(1)–O(12A)	168.19(7)	N(31)–Zn(1)–N(14A)	100.21(8)
O(33)–Zn(1)–O(12A)	90.84(7)	O(33)–Zn(1)–N(14A)	90.53(8)
O(12A)–Zn(1)–N(14A)	77.26(8)		

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The crystal structure of **6** shows a 1:1.5 ratio between zinc and ligand **3**, the same as that seen in **5** for zinc and ligand **2**. Again as was seen in **5**, the zinc coordination sphere is comprised of three chelating amide groups; here the zinc atom sits on a 3-fold axis so all three amide groups are related to each other by symmetry (Fig. 10). (The aryl ring lies across a 2-fold axis that passes through the middle of that ring). The coordination of the amide functionality of the three independent ligands and the zinc(II) center results in a tripodal (conical) architecture (Figure 11). Each tripod is further connected to three other tripods giving rise to extended two-dimensional coordination sheets. The N–H atoms of the ligands hydrogen bond to the sulphate anion and the included water molecules⁴⁹ and serve to link the sheets into a 3D network. As was seen for ligand **2** in both complexes **4** and **5**, the coordination of ligand **3** to a metal has the expected marked effect on the conformation of the amide substituents with the {N(1)–C(2)–C(3)–O(3)} torsion angle being *ca.* 16° *cf.* *ca.* 171 and 144° in **3**.

Fig. 10 The unique portion of the cationic network in the structure of **6**. The zinc atom sits on a 3-fold axis, and a 2-fold axis passes through the centre of the aryl ring.

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226 **Fig. 11** Illustration of the tripod in **6** (left) and tripod connected to three others to form a 2D
 227 network (right).
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229 **Table 3.** Selected bond lengths (Å) and angles (°) for **6**.

Zn(1)–N(1)	2.152(2)	Zn(1)–O(3)	2.1142(17)
Zn(1)–N(1B)	2.152(2)	Zn(1)–O(3B)	2.1142(17)
Zn(1)–N(1C)	2.152(2)	Zn(1)–O(3C)	2.1142(17)
N(1)–Zn(1)–O(3)	78.32(7)	N(1)–Zn(1)–N(1B)	97.69(7)
N(1)–Zn(1)–O(3B)	96.29(8)	N(1)–Zn(1)–N(1C)	97.69(7)
N(1)–Zn(1)–O(3C)	165.86(7)	O(3)–Zn(1)–N(1B)	165.86(8)
O(3)–Zn(1)–O(3B)	88.57(7)	O(3)–Zn(1)–N(1C)	96.29(8)
O(3)–Zn(1)–O(3C)	88.57(7)	N(1B)–Zn(1)–O(3B)	78.32(7)
N(1B)–Zn(1)–N(1C)	97.69(7)	N(1B)–Zn(1)–O(3C)	96.29(8)
O(3B)–Zn(1)–N(1C)	165.86(7)	O(3B)–Zn(1)–O(3C)	88.57(7)
N(1C)–Zn(1)–O(3C)	78.32(7)		

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232 The crystal structure of **7** shows a 1:1.33 ratio between zinc and ligand **3**, in contrast to
 233 the 1:1.5 ratio seen in **6**. Interestingly, the three unique zinc centres show two different
 234 coordination spheres. Both Zn(1) and Zn(3) have octahedral coordination geometries
 235 comprised of three chelating amide groups (Fig 12), whereas Zn(2) has a five-coordinated
 236 distorted square-based pyramidal geometry comprised of two chelating amide groups and one

bromine atom ($\tau = 0.33$ with Br(1) in the apical site⁴⁵). In **7**, similar tripods to those observed in the structure of **6** are observed, involving Zn(1) and Zn(3) and the chelating amide groups. The two arms of the tripods are linked to adjacent tripods to form a 1-D polymeric chain along the b-axis. Each 1-D polymeric chain is linked to the adjacent chain via coordination of Zn(2) and the third arm of the tripod along the a-b plane to form a 2-D grid architecture along the a-axis (Fig 13). In common with its zinc sulphate analogue **6**, the extended structure of **6** is comprised of two-dimensional coordination sheets, that are cross-linked by N–H...Br hydrogen bonds⁴⁶ to form a 3D network. As was seen for ligand **2** in the structures of **4** and **5**, and for ligand **3** in the structure of **6**, the coordination to a metal has the expected marked effect on the conformation of the amide substituents with the {N–C–C–O} torsion angles here in **7** ranging between *ca.* 23 and 43° cf. values of *ca.* 171 and 144° in **3**.

Fig. 12 The unique portion of the cationic sheets in the structure of **7**.

Fig. 13 Illustration of the tripod in **7** (left) and connectivity of one tripod to the adjacent chain forming a 2D grid (right).

Table 4. Selected bond lengths (Å) and angles (°) for **7**.

Zn(1)–O(12)	2.131(3)	Zn(1)–N(14)	2.179(4)
Zn(1)–N(21)	2.157(4)	Zn(1)–O(23)	2.142(3)
Zn(1)–N(1B)	2.166(3)	Zn(1)–O(3B)	2.140(3)
Zn(2)–Br(1)	2.321(5)	Zn(2)–O(32)	2.184(4)
Zn(2)–N(34)	2.076(4)	Zn(2)–N(41)	2.111(9)
Zn(2)–O(43)	2.175(3)	Zn(3)–O(52)	2.136(3)
Zn(3)–N(54)	2.165(4)	Zn(3)–N(61)	2.145(4)
Zn(3)–O(63)	2.149(3)	Zn(3)–O(72C)	2.169(3)
Zn(3)–N(74C)	2.165(4)		
O(12)–Zn(1)–N(14)	77.29(13)	O(12)–Zn(1)–N(21)	161.94(14)
O(12)–Zn(1)–O(23)	86.58(12)	O(12)–Zn(1)–N(1B)	97.27(13)
O(12)–Zn(1)–O(3B)	88.12(12)	N(14)–Zn(1)–N(21)	96.79(15)
N(14)–Zn(1)–O(23)	97.21(14)	N(14)–Zn(1)–N(1B)	98.88(15)
N(14)–Zn(1)–O(3B)	164.48(14)	N(21)–Zn(1)–O(23)	77.16(13)
N(21)–Zn(1)–N(1B)	100.52(14)	N(21)–Zn(1)–O(3B)	98.71(14)
O(23)–Zn(1)–N(1B)	163.91(13)	O(23)–Zn(1)–O(3B)	87.05(12)
N(1B)–Zn(1)–O(3B)	77.50(12)	Br(1)–Zn(2)–O(32)	103.55(19)
Br(1)–Zn(2)–N(34)	129.3(3)	Br(1)–Zn(2)–N(41)	113.9(5)
Br(1)–Zn(2)–O(43)	107.35(17)	O(32)–Zn(2)–N(34)	79.19(17)
O(32)–Zn(2)–N(41)	86.7(2)	O(32)–Zn(2)–O(42)	148.83(17)
N(34)–Zn(2)–N(41)	116.8(4)	N(34)–Zn(2)–O(43)	84.43(18)
N(41)–Zn(2)–O(43)	77.3(2)	O(52)–Zn(3)–N(54)	78.75(13)
O(52)–Zn(3)–N(61)	160.98(14)	O(52)–Zn(3)–O(63)	84.72(12)
O(52)–Zn(3)–O(72C)	89.06(12)	O(52)–Zn(3)–N(74C)	96.87(14)

N(54)–Zn(3)–N(61)	95.41(15)	N(54)–Zn(3)–O(63)	98.77(14)
N(54)–Zn(3)–O(72C)	165.68(14)	N(54)–Zn(3)–N(74C)	96.63(15)
N(61)–Zn(3)–O(63)	78.25(13)	N(61)–Zn(3)–O(72C)	98.49(14)
N(61)–Zn(3)–N(74C)	101.80(15)	O(63)–Zn(3)–O(72C)	87.43(12)
O(63)–Zn(3)–N(74C)	164.53(14)	O(72C)–Zn(3)–N(74C)	77.23(13)

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257 As mentioned above, there is a marked difference on the conformation of the amide
258 substituents of all the coordination polymers studied here. In **6** and **7** three ligands are
259 coordinated to the metal to form tripodal architectures. Interestingly, similar coordination
260 environment are found in **5**, but the bulky benzyl group of the ligand (*cf.* the isopropyl group
261 in **6** and **7**) around the metal centre seems to hinder the formation of the tripod. Thus,
262 alteration of the substituents in the molecular structure of the ligands (aryl/aliphatic) can
263 induce a drastic change in the final architecture of the networks. On the other hand, the nature
264 of the counteranions (tetrahedral sulphate and spherical bromide) also has an effect on the
265 final architectures. The anions can either be coordinated to the metal centre or interact with
266 the ligands via non-covalent interactions (mainly electrostatic and hydrogen bonding). With
267 ligand **2**, we were able to switch from a 1D coordination polymer (**4**) to a 3D coordination
268 network (**5**) when changing from ZnSO₄ to ZnBr₂. In the case of ligand **3**, coordination to
269 both ZnSO₄ and ZnBr₂ yielded polymeric 2D coordination sheets. However, the detailed
270 structure of these networks is considerably different, with ZnBr₂ giving a structure comprised
271 of three unique Zn centres in the “monomeric unit” and with bromide coordinating to zinc, in
272 contrast to the structure with ZnSO₄ where the anion interacts via electrostatic/hydrogen
273 bonding interactions to the ligand framework but does not coordinate to the metal centres.

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275 **Thermogravimetric Analysis (TGA).** Thermogravimetric (TG) analyses for compounds **4-7**
276 were carried out and the corresponding TG curves obtained (see Figures S12-S15 in the
277 Supporting Information). TG data is in good agreement with the calculated values obtained

from the single-crystal X-ray data. Analysis of TG results revealed that all the water molecules, coordinated and uncoordinated to the metal centres, are released within the temperature range of 40.0-230.0 °C. In polymer **4**, the TGA result indicated a weight loss of 16.7% which corresponds to the loss of five water molecules and half a molecule of ethanol, which matches well with the calculated one (16.7%). Thus, the assignment of disordered EtOH molecule present as lattice included solvates in **4** on the basis of SQUEEZE calculations is further supported by TG data (see crystal structure description). In **5**, the weight loss of 7.5% which may be attributed to the loss of four water molecules and one ethanol molecule, is also in good agreement with the calculated value (6.7%). In **6**, a weight loss of 4.4% was observed due to the loss of three water molecules; this is consistent with the calculated value (4.0%). In **7**, the weight loss of 4.9% which can be attributed to the loss of three water molecules and one ethanol molecule, is also in good agreement with the calculated value (5.0%).

X-ray powder diffraction. In order to establish the crystalline phase purity of **4-7**, bulk crystalline samples of the three coordination networks were analysed by X-ray powder diffraction. The experimental diffraction pattern of each sample was compared with the corresponding simulated pattern obtained from the single-crystal X-ray data. These experiments confirmed the crystalline phase purity of **5** (see Figure S16 in the Supporting Information). However, this was not the case for **4**, **6** and **7** where the experimental pattern showed the sample to be amorphous; this might be due to the inconsistent loss of solvent molecules in these samples.

Conclusions

Two new phenyl-bridged bis-pseudopeptidic ligands (**2** and **3**) have been successfully synthesized. The X-ray crystal structures of these two compounds reveal significantly different structural features in the solid state. While ligand **2** (with benzyl substituents) yields hydrogen bonded sheets, the structure of ligand **3** (with isopropyl substituents) reveals the formation of a hydrogen bonded three dimensional network. The coordination chemistry of these two ligands toward a range of zinc(II) salts has been explored and four novel coordination polymers/networks have been structurally characterised. The structures of these zinc(II) complexes differ considerably depending on the ligands' substituents and the counterion present. With ZnBr_2 and ligand **2**, a 3D coordination network (**5**) is formed while the same ligand with ZnSO_4 yields a 3D network generated by 1D coordination chains bridged by hydrogen bonds to sulphate counterions (**4**). Coordination of ligand **3** to ZnSO_4 and ZnBr_2 yielded 2D coordination layered sheet structures (**6** and **7**); anion-mediated hydrogen bonding between the 2D coordination layers is observed yielding the corresponding 3D networks. These results highlight the importance that specific structural features on the ligand (isopropyl vs. phenyl) and the nature of the counterions (sulphate vs. bromide) have on the final structure of the coordination polymers.

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Experimental Details

Instrumentation.

FT-IR spectra were recorded using PERKIN-ELMER Spectrum 100 IR with the ATR adapter. Microanalyses were performed on a Exeter Analytical CE-440 elemental analyser. Powder X-ray patterns were recorded on D4 Endeavor, Bruker-AXS (CuK α radiation, λ = 1.5418 Å) diffractometer. Thermogravimetric analyses were performed on a TG-STD A Mettler Toledo (model TGA/SDTA851e/LF/1600). ^1H and ^{13}C NMR spectra were recorded on either a Varian INOVA 500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) or a Varian MERCURY 300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C).

Synthesis of ligands and coordination polymers.

Synthesis of 2. Z-L-Phe-OH (11.075 g, 37.0 mmol) and triethylamine (5.13 mL, 37.0 mmol) were dissolved in 200 mL of dry THF in a 500 mL round bottom flask. The reaction mixture was cooled in a salt/ice bath at -10 °C. Cooled ethyl chloroformate (3.65 mL, 37.0 mmol) was added dropwise with an addition funnel. When the addition was finished the reaction mixture was stirred at -10 °C for 30 min. To the anhydride formed in this reaction, which is very reactive and unstable, *p*-diaminobenzene (2.000g, 18.5 mmol) previously dissolved in dry THF (25 mL) was added dropwise over 15 min (it is important to add the diamine very slowly to maintain the temperature at -10 °C). The reaction mixture was kept at -10 °C for 2 hours and then stirred for further 3 hours by letting the reaction mixture warm up to room temperature. A white precipitate was formed which was filtered, washed with water and methanol and dried in a vacuum oven to yield a white solid that was characterised as the Cbz-protected version of compound 2. Yield: 53% (6.528 g, 9.73 mmol). mp 251-252°C; $[\alpha]_{\text{D}}^{25} =$

349 44.04 (c = 0.01, DMSO); IR (ATR) 3294, 3031, 1691, 1659, 1519 cm^{-1} ; ^1H -NMR (500 MHz,
 350 DMSO- d_6) δ 2.75 – 2.92 (2H, m), 3.01 (2H, d, J = 13.4 Hz), 4.39 (2H, s), 4.95 (4H, s), 7.07 –
 351 7.41 (20H, m), 7.51 (4H, s), 7.63 (2H, d, J = 8.2 Hz), 10.03 (2H, s) ppm; ^{13}C -NMR (75 MHz,
 352 DMSO- d_6) δ 38.29, 57.57, 66.01, 120.45, 127.03, 128.22, 128.39, 128.75, 128.97, 129.93,
 353 135.10, 137.66, 138.54, 156.63, 170.88 ppm. HRMS (ESI-TOF) $^+$ calc for $\text{C}_{40}\text{H}_{38}\text{N}_4\text{O}_6$
 354 $(\text{M}+\text{H})^+$: 693.2689; found 693.2691. Anal. Calcd. for $\text{C}_{40}\text{H}_{38}\text{N}_4\text{O}_6$: C, 71.63; H, 5.71; N, 8.35.
 355 Found: C, 71.3; H, 5.6; N, 8.6. **Deprotection of 2-Cbz.** The resulting Cbz-protected
 356 pseudopeptide **2** (3.220 g, 4.80 mmol) was placed in a 100 mL round bottom flask. Then 30
 357 mL of HBr/AcOH (33%) were added. The resulting yellow solution was stirred under a
 358 nitrogen atmosphere for 1 h. The colourless solution was poured into a 250 mL breaker
 359 containing 100 mL of diethyl ether. The white precipitate formed was filtered and washed
 360 with diethyl ether. The solid was redissolved in 50 mL of distilled water and the resulting
 361 aqueous phase washed twice with 25 mL CHCl_3 . The aqueous phase was basified with solid
 362 NaOH to pH 12-13 and then NaCl was added until saturation. The aqueous solution was
 363 extracted 3 times with 50 mL of CHCl_3 and the organic phase was dried with anhydrous
 364 MgSO_4 . After filtering off the MgSO_4 , the solvent was removed under reduced pressure and
 365 the resulting product dried under reduced pressure to yield pure **2** as a white solid. Yield:
 366 85% (1.645 g, 4.08 mmol). mp 198-199°C; $[\alpha]_D^{25}$ = 48.92 (c = 0.01, DMSO); IR (ATR) 3372,
 367 3252, 3144, 3060, 3027, 2919, 2857, 1642, 1550, 1514 cm^{-1} ; ^1H -NMR (500 MHz, CDCl_3) δ
 368 1.46 (4H, s), 2.79 (2H, dd, J = 9.5, 13.9 Hz), 3.38 (2H, dd, J = 3.9, 13.9 Hz), 3.73 (2H, dd, J
 369 = 3.9, 9.5 Hz), 7.20 – 7.38 (10H, m), 7.57 (4H, s), 9.38 (2H, s) ppm; ^{13}C -NMR (75 MHz,
 370 CDCl_3) δ 40.97, 57.00, 120.25, 127.16, 129.04, 129.51, 134.18, 137.96, 172.35 ppm. HRMS
 371 (ESI-TOF) $^+$ calc for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2$ $(\text{M}+\text{H})^+$: 404.2134; found 404.2134. Anal. Calcd. for
 372 $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2$: C, 71.62; H, 6.51; N, 13.92. Found: C, 71.4; H, 6.3; N, 14.2.

Synthesis of 3. This compound was prepared using the same protocol as that described for the synthesis of **2**. **Characterisation of 3-Cbz.** 40 % yield; mp 259-260 °C; $[\alpha]_D^{25} = 43.15$ (c = 0.01, DMSO); IR (ATR) 3290, 2961, 1689, 1657, 1530, 1517 cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 0.89 (12H, d, $J = 6.3$ Hz), 1.79 – 2.17 (2H, m), 3.97 (2H, t, $J = 7.8$ Hz), 5.03 (4H, s), 7.33 (10H, t, $J = 15.5$ Hz), 7.51 (4H, s), 9.95 (2H, s) ppm; $^{13}\text{C-NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ 18.90, 19.61, 30.81, 61.44, 65.88, 120.14, 128.11, 128.20, 128.76, 134.79, 137.49, 156.66, 170.56 ppm. HRMS (ESI-TOF) $^{+}$ calc for $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}_6$ ($\text{M}+\text{Na}$) $^{+}$: 597.2689; found 597.2689 Anal. Calcd. for $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}_6$: C, 66.88; H, 6.67; N, 9.75. Found: C, 66.6; H, 6.9; N, 9.5. **Characterisation of 3.** 94 % yield; mp 163-164°C; $[\alpha]_D^{25} = 30.55$ (c = 0.01, DMSO); IR (ATR) 3303, 2961, 1661, 1599, 1539, 1518, 1485 cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 0.86 (12H, dd, $J = 6.8, 35.6$ Hz), 1.76 (4H, s), 1.86 – 1.97 (2H, m), 3.06 (2H, d, $J = 5.4$ Hz), 7.53 (4H, s), 9.72 (2H, s) ppm; $^{13}\text{C-NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ 17.71, 20.05, 32.24, 61.16, 120.01, 134.73, 174.02 ppm. HRMS (ESI-TOF) $^{+}$ calc for $\text{C}_{16}\text{H}_{26}\text{N}_4\text{O}_2$ ($\text{M}+\text{H}$) $^{+}$: 307.2134; found 307.2136 Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{N}_4\text{O}_2$: C, 62.72; H, 8.55; N, 18.29. Found: C, 62.5; H, 8.7; N, 18.6.

Synthesis of $\{[\text{Zn}(\mathbf{2})](\text{SO}_4)\}_n$ (4). Coordination polymer **4** was synthesized by layering an ethanolic solution (10 mL) of ligand **2** (20.0 mg, 0.0497 mmol) over an aqueous solution (10 mL) of $\text{Zn}(\text{SO}_4)_2 \cdot 7 \text{H}_2\text{O}$ (14.3 mg, 0.0497 mmol). After a period of two weeks X-ray quality single crystals were obtained. Yield: 45 % (15 mg). Anal. Calcd. for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_6\text{SZn} \cdot 6 \text{H}_2\text{O} \cdot 0.5 \text{CH}_3\text{CH}_2\text{OH}$: C, 42.92; H, 5.72; N, 8.31. Found: C, 42.59; H, 5.26; N, 8.23. FT-IR (cm^{-1}): 3338, 3276, 3029, 2967, 2931, 1656, 1605, 1540, 1515, 1493, 1456, 1411.

Synthesis and crystallization of $\{[\text{Zn}(\mathbf{2})]\text{Br}_2\}_n$ (5). Coordination polymer **5** was synthesized by layering an ethanolic solution (10 mL) of ligand **2** (20.0 mg, 0.0497 mmol) over a aqueous solution (10 mL) of ZnBr_2 (11.2 mg, 0.0497 mmol). After a period of two weeks X-ray quality single crystals were obtained. Yield: 27% (8 mg). Anal. Calcd. for

398 $C_{72}H_{78}Br_4N_{12}O_6Zn_2 \cdot 5.5 H_2O \cdot 1.5 CH_3CH_2OH$: C, 49.33; H, 5.4; N, 9.20. Found: C, 49.42; H,
399 5.52; N, 9.13. FT-IR (cm^{-1}): 3304, 3255, 3192, 3057, 1653, 1579, 1537, 1512, 1498, 1455,
400 1416.

401 **Synthesis and crystallization of $\{[Zn(3)](SO_4)\}_n$ (6).** Coordination polymer **6** was
402 synthesized by layering an ethanolic solution (10 mL) of ligand **3** (20.0 mg, 0.0653 mmol)
403 over an aqueous solution (10 mL) of $Zn(SO_4)_2 \cdot 7 H_2O$ (18.8 mg, 0.0653 mmol). After a period
404 of two weeks X-ray quality single crystals were obtained. Yield: 42% (12 mg). Anal. Calcd.
405 for $C_{48}H_{78}N_{12}O_{14}S_2Zn_2 \cdot 7 H_2O$: C, 42.14; H, 6.78; N, 12.28. Found: C, 41.46; H, 6.23; N,
406 11.91. FT-IR (cm^{-1}): 3257, 2965, 1645, 1602, 1538, 1514, 1471, 1417.

407 **Synthesis and crystallization of $\{[Zn_3(3)_4Br](Br)_5\}_n$ (7).** Coordination polymer **7** was
408 synthesised by layering an ethanolic solution (5 mL) of ligand **2** (30.6 mg, 0.1 mmol) over an
409 aqueous solution (5 mL) of $ZnBr_2$ (22.5 mg, 0.1 mmol). After a period of one week X-ray
410 quality crystals were obtained. Yield 20% (10 mg). Anal. Calcd. for
411 $C_{64}H_{104}Br_6N_{16}O_8Zn_3 \cdot 2CH_3CH_2OH \cdot 3H_2O$: C, 39.89; H, 6.01; N, 10.95 found: C, 39.56; H,
412 6.37; N, 11.04. FT-IR (cm^{-1}): 3422, 3244, 3215, 2965, 1671, 1638, 1610, 1577, 1570, 1560,
413 1531, 1514, 1466, 1416, 1397, 1376, 1311, 1251, 1110.

414

415 **X-ray crystal structure determinations.**

416 Table 4 provides a summary of the crystallographic data for compounds **2**, **3**, **4**, **5**, **6** and **7**.
417 Data were collected using Oxford Diffraction Xcalibur PX Ultra (**2**, **3**, **5**, **6** and **7**) and
418 Xcalibur 3 (**4**) diffractometers, and the structures were refined based on F^2 using the
419 SHELXTL and SHELX-97 program systems.⁴⁷ The absolute structures of **3**, **4**, **5**, **6** and **7**
420 were determined by a combination of R -factor tests [for **3** $R_1^+ = 0.0271$, $R_1^- = 0.0273$; for **4**
421 $R_1^+ = 0.0636$, $R_1^- = 0.0819$; for **5** $R_1^+ = 0.0249$, $R_1^- = 0.0368$; for **6** $R_1^+ = 0.0324$, $R_1^- =$

422 0.0406; for **7** $R_1^+ = 0.0388$, $R_1^- = 0.0457$] and by use of the Flack parameter [for **3** $x^+ =$
423 $+0.02(17)$, $x^- = +0.98(17)$; for **4** $x^+ = +0.042(9)$, $x^- = +0.958(9)$; for **5** $x^+ = +0.000(12)$, $x^- =$
424 $+1.009(12)$; for **6** $x^+ = +0.02(3)$, $x^- = +0.98(3)$; for **7** $x^+ = +0.004(15)$, $x^- = +0.996(15)$]. The
425 absolute structure of **2** could not be unambiguously determined by either *R*-factor tests [$R_1^+ =$
426 0.0648 , $R_1^- = 0.0648$] or by use of the Flack parameter [$x^+ = +0.0(4)$, $x^- = +1.0(4)$] and so
427 was assigned based on internal reference on the C2 and C13 centres. CCDC 826892 to
428 826896 (for **2** to **6**) and 828392 (for **7**)

Table 4. Crystal Data, Data Collection and Refinement Parameters for compounds **2**, **3**, **4**, **5**, **6** and **7**.

Data	2	3	4	5	6	7
formula	C ₂₄ H ₂₆ N ₄ O ₂	C ₁₆ H ₂₆ N ₄ O ₂	[C ₂₄ H ₃₀ N ₄ O ₄ Zn](SO ₄)	[C ₃₆ H ₃₉ N ₆ O ₃ Zn](Br) ₂	[C ₂₄ H ₃₉ N ₆ O ₃ Zn](SO ₄) ¹⁹ / ₁₂ (H ₂ O)	[C ₆₄ H ₁₀₄ BrN ₁₆ O ₈ Zn ₃](Br) ₅
solvent	—	—	2.25(H ₂ O)·0.5EtOH	2(H ₂ O)·0.5(C ₂ H ₆ O)	—	7H ₂ O·6EtOH
formula weight	402.49	306.41	663.52	887.99	649.57	2303.72
colour, habit	colourless tabular needles	colourless platy needles	colourless blocks	colourless blocks	colourless blocks	colourless platy needles
crystal size / mm³	0.33 x 0.12 x 0.03	0.25 x 0.23 x 0.08	0.64 x 0.31 x 0.13	0.21 x 0.16 x 0.12	0.32 x 0.17 x 0.16	0.32 · 0.11 · 0.02
temperature / K	173	173	173	173	173	173
crystal system	monoclinic	monoclinic	orthorhombic	trigonal	rhombohedral	monoclinic
space group	<i>P</i> 2 ₁ (no. 4)	<i>P</i> 2 ₁ (no. 4)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	<i>P</i> 3 ₁ 21 (no. 152)	<i>R</i> 32 (no. 155)	<i>C</i> 2 (no. 5)
<i>a</i> / Å	5.4867(2)	5.22808(5)	13.9923(2)	13.37139(6)	11.63262(9)	39.030(2)
<i>b</i> / Å	42.1629(16)	9.49693(9)	14.3096(2)	—	—	11.8817(2)
<i>c</i> / Å	9.0036(3)	16.70757(16)	32.6979(5)	41.4227(2)	39.8175(3)	27.6330(13)
β / deg	90.131(4)	95.6549(9)	—	—	—	123.780(7)
<i>V</i> / Å³	2082.84(13)	825.506(14)	6546.91(16)	6413.89(5)	4666.16(6)	10651.2(12)
<i>Z</i>	4 [a]	2	8 [a]	6	6 [b]	4
<i>D</i>_c / g cm⁻³	1.284	1.233	1.346	1.379	1.387	1.437
radiation used	Cu-Kα	Cu-Kα	Mo-Kα	Cu-Kα	Cu-Kα	Cu-Kα
μ / mm⁻¹	0.667	0.668	0.871	3.364	2.198	3.972
2θ max / deg	137	145	65	137	145	148
no. of unique reflns						
measured (<i>R</i>_{int})	7202 (0.0466)	3245 (0.0258)	21753 (0.0434)	7876 (0.0312)	2067 (0.0138)	18211 (0.0364)
obs, <i>F</i>_o > 4σ(<i>F</i>_o)	6896	3138	17574	7782	2064	16436
no. of variables	589	224	756	512	156	915
<i>R</i>₁(obs), <i>wR</i>₂(all) [c]	0.0648, 0.1614	0.0271, 0.0717	0.0636, 0.1680	0.0249, 0.0772	0.0324, 0.0928	0.0388, 0.1085

[a] There are two crystallographically independent “molecules” in the asymmetric unit. [b] The structure has *C*₃ symmetry. [c] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

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44. The eight intermolecular N–H···O hydrogen bonds have the following geometries [N···O Å, H···O Å, N–H···O °]; N(1A)–H···O(12B) 3.109(5), 2.25, 160; N(4A)–H···O(12B) 2.870(4), 1.98, 169; N(11A)–H···O(3B) 3.128(5), 2.30, 153; N(14A)–H···O(3B) 3.185(5), 2.30, 169; N(1B)–H···O(12A) 3.134(5), 2.27, 162; N(4B)–H···O(12A) 2.882(4), 2.02, 160; N(11B)–H···O(3A) 3.153(5), 2.32, 155; N(14B)–H···O(3A) 3.153(5), 2.29, 161.
45. The intramolecular N(1)–H···O(3) hydrogen bonds have the following geometries [N···O Å, H···O Å, N–H···O °]; N(1A)–H···O(3A) 2.956(5), 2.54, 109; N(1B)–H···O(3B) 2.955(5), 2.57, 107.
46. The four intermolecular N–H···O hydrogen bonds have the following geometries [N···O Å, H···O Å, N–H···O °]; N(1)–H···O(3) 3.1641(18), 2.30, 161; N(4)–H···O(3) 3.1673(14), 2.38, 146; N(11)–H···O(12) 3.1224(13), 2.40, 137; N(14)–H···O(12) 3.1389(16), 2.30, 156.
47. The N···O and O···O hydrogen bonds have the following heteroatom separations (Å); N(1A)···O(61) 2.939(5), N(4A)···O(41) 2.817(4), N(11A)···O(62) 2.882(4), O(29A)···O(52) 2.698(5), O(30A)···O(52) 2.703(5), O(30A)···O(61) 2.779(5), N(1B)···O(63) 2.924(5), N(4B)···O(51) 2.914(5), N(11B)···O(53) 2.820(5), N(14B)···O(64)

2.907(6), O(29B)···O(41) 2.699(4), O(29B)···O(64) 2.750(5), O(30B)···O(43) 2.758(4), O(43)···O(62) 2.714(4), O(44)···O(63) 2.745(5), O(44)···O(64) 2.766(5), O(52)···O(65) 3.097(11), O(54)···O(61) 2.905(8), O(62)···O(63) 2.829(4). [The O(4x) and O(5x) atoms are part of the two unique sulphate groups, and the O(6x) atoms are part of the included water molecules.] Note that none of the N–H or O–H hydrogen atoms of the ligands or solvent molecules could be located, so the hydrogen bonds have been inferred by consideration of both the heteroatom separations and the geometries subtended at the heteroatoms by the vectors of the contacts. Additionally there were further highly disordered solvent molecules which were not included in the coordinate list. However, being highly disordered makes them unlikely to be involved in significant intermolecular interactions. That one of the sulphate anions is also disordered complicates matters further; see supporting information for more details.

48. The N–H···O and N–H···Br hydrogen bonds have the following geometries [N···X Å, H···X Å, N–H···X °]; N(1)–H···Br(2) 3.302(2), 2.44, 162; N(4)–H···Br(2) 3.340(2), 2.45, 169; N(11)–H···O(60) 2.826(3), 1.93, 177; N(14)–H···Br(1) 3.627(2), 2.89, 140; N(31)–H···Br(1) 3.520(2), 2.62, 174; N(31)–H···Br(2) 3.555(2), 2.89, 132; N(34)–H···Br(1) 3.387(2), 2.49, 174. The bromide anions additionally link to the included water molecules, which also link to themselves; the O···Br and O···O heteroatom separations (Å) are O(50)···Br(1) 3.375(3), O(50)···Br(2) 3.371(3), O(50)···O(60) 2.824(4) [though the hydrogen atoms of the water molecules could not be located, their presence has been inferred from the heteroatom separations].

49. The N–H···O hydrogen bonds have the following geometries [N···O Å, H···O Å, N–H···O °]; N(1)–H···O(30) 3.114(5), 2.36, 141; N(1)–H···O(22) 3.017(3), 2.14, 166; N(4)–H···O(21) 3.043(2), 2.18, 162 (the O(2x) atoms are part of the sulphate group, and O(30) is the included water molecule).