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PAPER

Metal-directed assembly of chiral bis-Zn(II) Schiff base structures†

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Tetra-Schiff bases derived from (chiral) bis-salphen ligand scaffolds furnish, upon metalation with appropriate metal reagents, their multinuclear structures with associated $Zn(OAc)_2$ or $Zn(OH)_2$ fragments. The tendency of retaining these salts was investigated using four different (chiral) bis-salphen scaffolds. The presence of the additional Zn ions was supported by NMR studies, mass determinations and X-ray crystallography showing in two cases the possible mode of coordination within these multinuclear structures. In one case, dimerization of the Zn_3 complex leads to a unique hexanuclear Zn_6 complex being a mixture of diastereoisomeric complexes as revealed by NMR spectroscopy.

Introduction

Schiff base structures find use in numerous areas of academic research including the design and synthesis of magnetic materials,[1] homogeneous catalysis,[2] multinuclear (cluster) compounds with interesting photophysical and/or electronic features,[3] supramolecular chemistry,[4] and sensing devices.[5] One major advantage of using Schiff base systems is their relative easy synthesis that stems from the well-known condensation reaction between a ketone or aldehyde combined with an amine reagent. The synthesis of compounds comprising multiple imine bonds within the targeted structure has the intrinsic difficulty that isolation and purification may be hampered by the reversible nature of the imine bond.[6] Therefore, a solution often used to prevent undesired imine hydrolysis or equilibration of distinct imine bonds within the same Schiff base framework is the use of metal templation or stable ketimine intermediates.[7] The imine coordination to metal ions indeed has proven to be a highly effective tool for the selective isolation of, for instance, macrocyclic[8] and other types of multinuclear Schiff base complexes.[9]

As part of our ongoing activities with multinuclear salphen [salphen = *N*,*N*′-phenylene-1,2-bis(salicylimine)] structures, we recently reported on the use of biphenyl-bridged bis-Zn(salphen)s.[10] These complexes have two distinct chiral conformations (with *P*- or *M*-helicity) that interconvert in the absence of strongly coordinating ditopic ligands. The use of these systems as hosts for chiral carboxylic acids in supramolecular chirogenesis was effectively demonstrated. The operative mechanism in the creation of supramolecular chirality in this host system is the exchange of a formally associated HOAc molecule (Fig. 1) for chiral acids. This HOAc originates from the synthesis of the host that involves metalation of the *in situ* formed bis-salphen ligand by zinc acetate dihydrate; the isolated product contains one molecule of HOAc of which the unusual binding was confirmed by MS, X-ray crystallography and various 1D and 2D NMR spectroscopic methods. This HOAc molecule is in fact split into a bridging acetate binding to both Zn(II) centers of the host molecules, whereas the residual proton is involved in hydrogen binding to the interior phenolic O-atoms. This structural motif was supported (in part) by X-ray diffraction studies, and a detailed DFT analysis revealed the preferential location of the proton. The intramolecularly associated HOAc can be regarded as a directing agent to yield the bis-metalated structure after work-up. Of particular note is the fact that the bis-salphen scaffold could not be formed and/or isolated in the absence of the Zn salt and thus the latter is also a prerequisite to access these kinds of host systems.

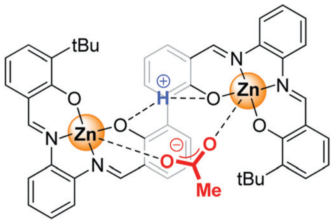

Fig. 1 A bis-Zn(salphen) complex with an associated HOAc molecule (red and blue fragments) in an unusual intramolecular binding mode.[10]

We were wondering whether this directing effect is of a more general nature since more effective host systems for chirogenesis applications are foreseen that do not incorporate such salts that likely compete for substrate binding.[11] Hence we have investigated the formation of structurally analogous (chiral) bis-Zn-

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(salphen)s under comparable reaction conditions. Our new results have revealed that, unlike for the previously reported system,[10] these structures comprise one molecule of the *metal* reagent (rather than HOAc) once isolated and their inclusion is facilitated through Zn–O coordination motifs. The interaction of the Zn(II) salt in these new structures has been investigated in detail using 1D and 2D NMR, DOSY, mass spectrometry, and X-ray diffraction studies. A possible explanation for the observed differences in these template reactions is put forward, and the data should allow for more efficient designs of supramolecular host systems with interesting binding properties for a wide range of ditopic ligands useful in chirality sensing applications.

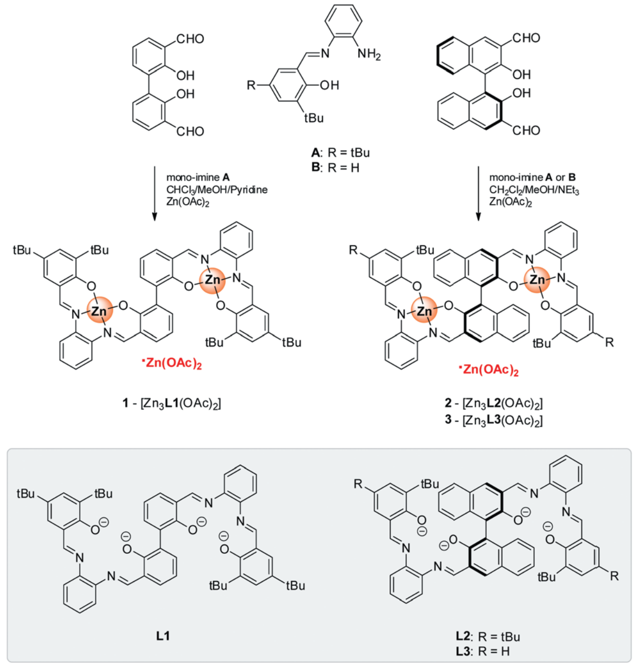
Results and discussion

The reaction conditions for the construction of bis-Zn(salphen)s of the type shown in Fig. 1 allow for direct synthesis of the metalated bis-salphen structures by treatment of bis-aldehydes with appropriate mono-imine (half-salphen) reagents (**A** and **B**, Scheme 1) in the presence of $Zn(OAc)_2$. In order to assess whether the unique binding of HOAc is also observed for other, differently substituted bis-Zn(salphen)s we first used mono-imine reagent **A** to prepare complex **1**. The only difference of this complex (**1**) with the previously reported HOAc-containing species (Fig. 1) is the presence of two additional *t*Bu groups on the bis-salphen scaffold. Complex **1** was isolated as an orange solid (47%) and was first analyzed by NMR spectroscopy and MALDI(+) mass spectrometry. Interestingly, the compound did not contain an associated HOAc but instead one molecule of $Zn(OAc)_2$ (presumably coordinating to the other Zn centers *via* bridging acetates). The molecular formula can thus be abbreviated as $[Zn_3\mathbf{L1}(OAc)_2]$ where **L1** stands for the bis-salphen ligand scaffold (see Scheme 1). In order to see whether other ligand scaffolds (**L2** and **L3**) would generate similar trinuclear compositions, we also used the chiral reagent (*S*)-2,2′-dihydroxy-[1,1′-binaphthalene]-3,3′-dialdehyde and reacted this with mono-imines **A** and **B** in the presence of a slight excess of $Zn(OAc)_2$; this afforded the trinuclear complexes $[Zn_3\mathbf{L2}(OAc)_2]$ **2** and $[Zn_3\mathbf{L3}(OAc)_2]$ **3** in 43% and 61% isolated yield, respectively.

The ^1H NMR spectra of $[Zn_3\mathbf{L1}(OAc)_2]$ **1**, $[Zn_3\mathbf{L2}(OAc)_2]$ **2** and $[Zn_3\mathbf{L3}(OAc)_2]$ **3** recorded in either d_6-DMSO or d_6-acetone show the presence of a characteristic singlet resonance at $\delta \sim 1.80$ ppm (in d_6-DMSO) corresponding to six protons (OAc fragments) by signal integration compared to four CH=N protons of the respective ligand scaffold. Note that "free" uncoordinated $Zn(OAc)_2$ also provides a peak at 1.80 ppm in this deuterated solvent. Therefore, one can conclude that under these polar conditions these supramolecular assemblies dissociate into the individual components.

Furthermore, in the MALDI(+) mass spectra, clear evidence for the formation of these $Zn(OAc)_2$-associated species was found as in all three cases a molecular ion peak was observed. As an illustrative example, Fig. 2 displays the observed and calculated isotopic pattern for $[Zn_3\mathbf{L2}(OAc)_2]$ **2**; as can be clearly noted, the presence of multiple Zn ions in the structure provides a spectrometric signature that is easily recognized and therefore allows, in combination with the NMR data, fast identification of the molecular formula.

Although the molecular composition of complexes $[Zn_3\mathbf{L}(OAc)_2]$ **1–3** could thus be easily established, the possible coordination mode of the $Zn(OAc)_2$ to the Zn(II) centers in these bis-Zn(salphen)s could not be easily deduced with these data. Fortunately, we were able to grow single crystalline material for trinuclear $[Zn_3\mathbf{L1}(OAc)_2]$ **1** in the presence of hexylamine, and the structure that was determined by X-ray crystallography is shown in Fig. 3. The structure comprises the bis-Zn(salphen) complex that is axially coordinated on one side by a hexylamine,



Scheme 1 Synthesis of trinuclear complexes $[Zn_3\mathbf{L}(OAc)_2]$ **1–3** where **L** = **L1**, **L2** or **L3**.

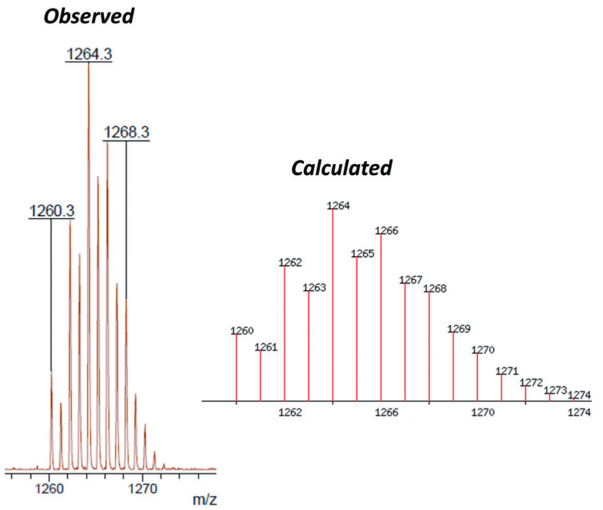


Fig. 2 Observed and calculated isotopic pattern for $[M^+]$ related to the molecular formula $C_{70}H_{72}N_4O_{10}Zn_3$; this formula corresponds to the proposed composition for complex $[Zn_3\mathbf{L2}(OAc)_2]$ **2** depicted in Scheme 1.

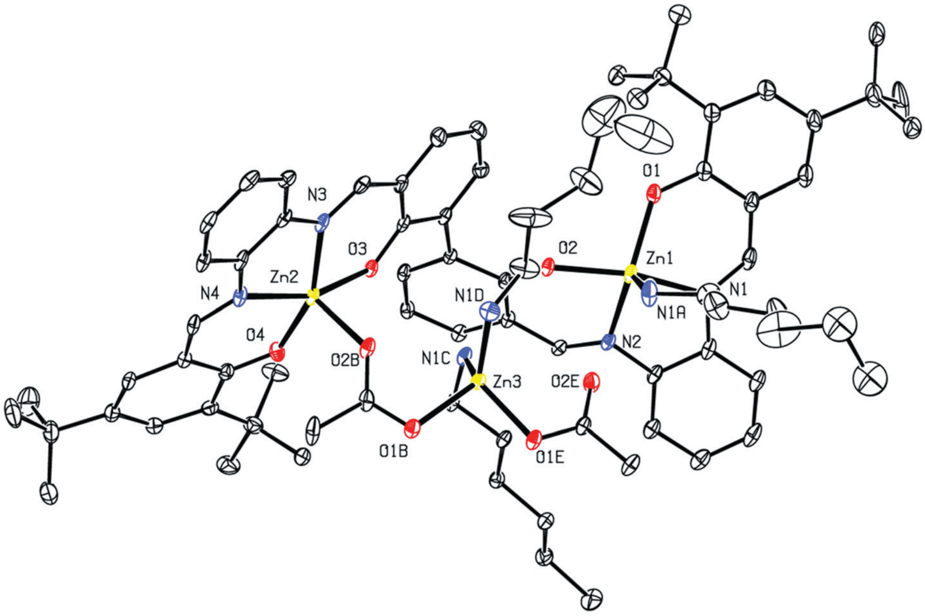
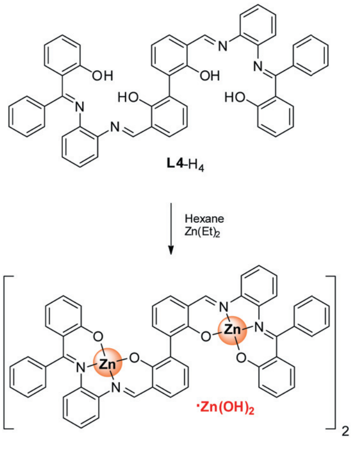


Fig. 3 X-ray molecular structure (ellipsoids drawn at 30% probability for clarity) determined for **1** upon crystallization in the presence of hexylamine. H-atoms and co-crystallized solvent molecules are omitted for clarity as well as part of the disorder in one of the hexylamines and *t*Bu groups. Selected bond lengths (Å) and angles (°), esd's in parentheses: Zn(2)–O(3) = 1.976(3), Zn(2)–O(4) = 1.971(5), Zn(2)–O(2B) = 2.044(4), Zn(2)–N(3) = 2.090(6), Zn(2)–N(4) = 2.081(4), Zn(3)–N(1C) = 2.015(5), Zn(3)–N(1D) = 2.038(7), Zn(3)–O(1B) = 2.004(4), Zn(3)–O(1E) = 1.973(4); O(4)–Zn(2)–O(3) = 97.77(17), N(4)–Zn(2)–N(3) = 77.5(2), N(4)–Zn(2)–O(2B) = 104.54(16), O(3)–Zn(2)–O(2B) = 93.17(14), N(1C)–Zn(3)–N(1D) = 108.4(2), O(1B)–Zn(3)–O(1E) = 93.79(15).



4 - [Zn$_3$**L4**(OH)$_2$]$_2$

Scheme 2 Synthesis of hexanuclear complex [Zn$_3$**L4**(OH)$_2$]$_2$ **4** from precursor ligand **L4**-H$_4$.

while the other Zn ion is coordinated by a bridging acetate. The latter is also connected to a third Zn center that has two hexylamine ligands and a monodentate OAc anion associated.

Although the structure shows that the Zn(OAc)$_2$ unit is here not acting as an intramolecular bridge between the two Zn(salphen)s, under relatively non-polar conditions such a bridging nature cannot be ruled out. Also, the presence of a competing amine can affect a possible bidentate and/or bridging mode.

Then, a different bis-salphen scaffold **L4**-H$_4$ (Scheme 2) was probed which contains two ketimine fragments that allow for isolation of the free base ligand and subsequent metalation with a different Zn reagent (ZnEt$_2$); this should prevent any inclusion of a Zn salt after isolation of the product.[11] Thus the bis-salphen ligand precursor **L4**-H$_4$ was treated with ZnEt$_2$ in hexane resulting in immediate precipitation of an orange solid. Analysis of this product (*i.e.*, complex [Zn$_3$**L4**(OH)$_2$]$_2$ **4**) was done by NMR spectroscopy and MALDI(+)-MS. Interestingly, the ^{1}H NMR spectrum recorded for [Zn$_3$**L4**(OH)$_2$]$_2$ **4** in CD$_2$Cl$_2$ showed the presence of two separate signals for the imine-H at δ = 8.08 and 8.79 ppm respectively. More surprisingly, two high-field singlet resonances were observed at δ = −0.64 and 0.12 ppm that were tentatively assigned to OH groups (Fig. 5). The ^{13}C{^{1}H} also showed the presence of a more complicated species (see ESI†).

In order to elucidate the identity of the product isolated and to compare the analytical data with those gathered for complexes **1–3**, X-ray diffraction studies were undertaken (Fig. 4). The structure of [Zn$_3$**L4**(OH)$_2$]$_2$ **4** comprises a hexanuclear Zn$_6$ complex having two bis-Zn(salphen)s interconnected through two additional Zn ions and four hydroxo (OH) bridging ligands. The molecule therefore could be regarded as a "bis-Zn-(OH)$_2$" coordination complex. We believe that the Zn(OH)$_2$ units originate from the synthetic procedure and likely is the result of partial hydrolysis of the ZnEt$_2$ before and/or during work-up and subsequent combination with the product upon precipitation.

In each crystallographically independent unit, each Zn ion [for example, Zn(1) in Fig. 4] present in the salphen coordination pocket is surrounded by the tetradentate N$_2$O$_2$ ligand and axially coordinated by an OH anion [O(6)] which in turn bridges to an "external" Zn center [Zn(3)]. This Zn(3) is coordinated by three salphen O-atoms from the bis-salphen scaffold (two from one

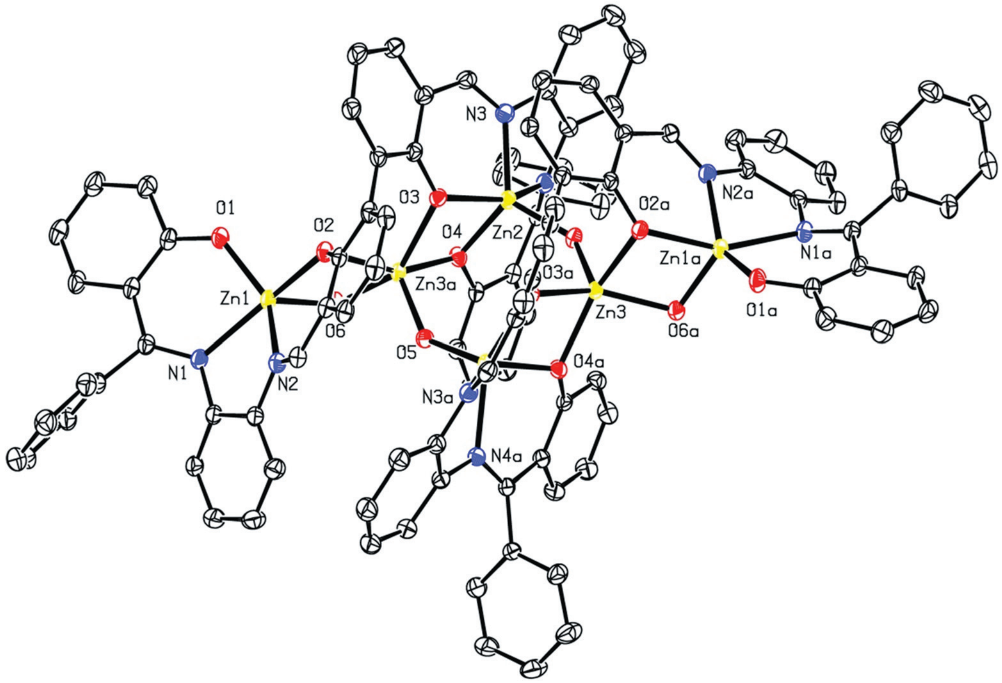


Fig. 4 X-ray molecular structure (ellipsoids drawn at 50% probability) determined for **4**; H-atoms and co-crystallized solvent molecules are omitted for clarity and only a partial numbering scheme is presented. The disorder in the co-crystallized solvent molecules (DCM and DCE) is not shown here. Selected bond lengths (Å) and angles (°), esd's in parentheses: Zn(1)–O(1) = 1.9445(17), Zn(1)–(O2) = 2.0963(15), Zn(1)–O(6) = 1.9573(17), Zn(1)–N(1) = 2.1613(19), Zn(1)–N(2) = 2.097(2), Zn(3)–O(4) = 2.0682(16), Zn(3)–O(6) = 1.9934(16), Zn(3)–O(2) = 2.1375(16), Zn(3)–O(3) = 2.0813(16), Zn(3)–O(5) = 1.9492(16); N(1)–Zn(1)–N(2) = 76.91(7), O(1)–Zn(1)–O(2) = 99.06(7), N(1)–Zn(1)–O(1) = 88.64(7), N(1)–Zn(1)–O(2) = 157.28(7), N(1)–Zn(1)–O(6) = 116.42(7), O(4)–Zn(3)–O(6) = 97.95(7), O(3)–Zn(3)–O(6) = 145.85(7), O(2)–Zn(3)–O(6) = 79.89(6).

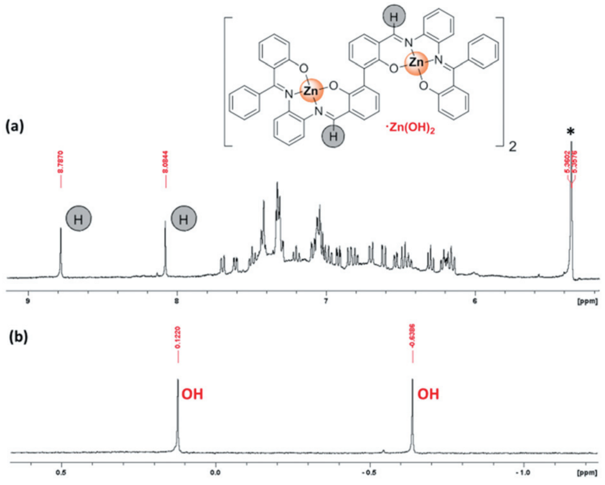
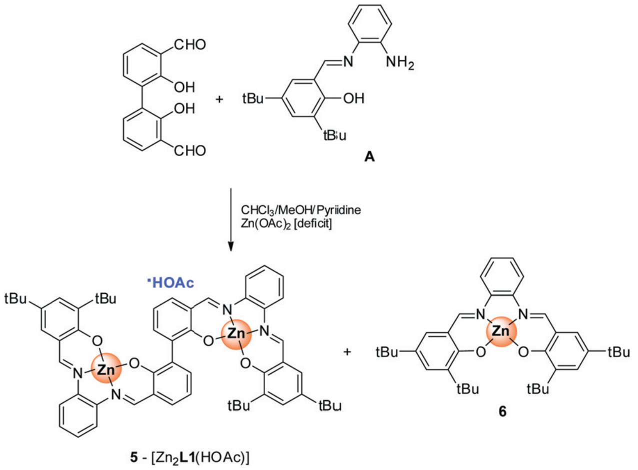


Fig. 5 Selected NMR regions (CD_2Cl_2) for complex $[Zn_3\mathbf{L4}(OH)_2]_2$ **4** and partial peak assignment: (a) aromatic region (5–9 ppm) and (b) aliphatic region (−1 to −0.5 ppm). The asterisk denotes the residual solvent signal.

salphen and one from another salphen fragment) and a second OH anion coordinated to Zn(3) then allows for connecting both "Zn_3" parts to assemble into the hexanuclear species. Note that in both bis-salphen scaffolds there is a biphenyl spacer that can have two distinct chiral conformations having either *M* or *P*-helicity.[10]

Obviously the bis-Zn(salphen) complex exists as a racemate, though in the solid state we observed only one of the possible diastereoisomers with both biphenyl fragments having *M*-helicity (or *R*-configuration). A comparison between the solid state features and the NMR data for $[Zn_3\mathbf{L4}(OH)_2]_2$ **4** reveals that the assembly is stable in solution as two sets of resonances are noted (Fig. 5). The presence of two distinct high-field singlets at $\delta = -0.64$ and 0.12 ppm (*vide supra*, and Fig. 5b) ascribed to the OH anions and two imine-H at $\delta = 8.79$ and 8.08 ppm is thus consistent with the fact that the hexanuclear assembly is retained in solution as the individual components would give rise to only one observable imine and one OH resonance. Further evidence for this was provided by a DOSY NMR experiment (ESI†) carried out in CD_2Cl_2: the hydrodynamic diameter that was calculated (~14 Å) reasonably fits with the minimal diameter of around 12 Å of the hexanuclear aggregate $[Zn_3\mathbf{L4}(OH)_2]_2$ **4** as observed in the solid state (Fig. 4). Note that an exact fit is not feasible due to the ellipsoidal nature of the complex.

In order to understand which factors control the formation of the multinuclear Zn-complexes **1–4** *versus* the HOAc-associated bis-Zn(salphen)s reported previously (Fig. 1),[10] we closely examined the reaction stoichiometry. In all the present examples (complexes **1–4**) a (slight) excess of Zn reagent was used whereas the HOAc-containing complex (Fig. 1) was prepared in the presence of a slight deficit of $Zn(OAc)_2$. This difference could therefore be decisive in the formation of either the HOAc- or the $Zn(OAc)_2$-associated containing structures. To further test



Scheme 3 Synthesis of HOAc-complex $[Zn_2\mathbf{L1}(HOAc)]$ **5** and side-product **6**.

this hypothesis, we combined 3,3′-diformyl-2,2′-dihydroxy-1,1′-biphenyl (Scheme 3) with mono-imine **A** in the presence of a slight *deficit* of $Zn(OAc)_2$ using similar reaction conditions as reported for $[Zn_3\mathbf{L1}(OAc)_2]$ **1** (Experimental section). An orange solid was isolated that was analyzed by ^1H NMR spectroscopy; comparison with authentic data revealed the presence of two species, *viz.* binuclear complex $[Zn_2\mathbf{L1}(HOAc)]$ **5** and the known mononuclear Zn(salphen) derivative **6**[12] in a 1 : 1.3 ratio (see ESI†). Recrystallization from warm MeOH afforded pure $[Zn_2\mathbf{L1}(HOAc)]$ **5** that was identified as a bis-Zn(salphen) complex with one molecule of associated HOAc; this is supported by the relative integral ratio between the imine-H of the binuclear host (4H) and the HOAc resonance at $\delta = 1.90$ ppm (3H). Furthermore, there is a clear difference in chemical shift ($\delta = 1.90$ ppm for $[Zn_2\mathbf{L1}(HOAc)]$) as opposed to the OAc fragments in complex $[Zn_3\mathbf{L1}(OAc)_2]$ **1** ($\delta = 1.81$ ppm, see ESI†). Also, the ^{13}C NMR analysis showed a significant difference between trinuclear $[Zn_3\mathbf{L1}(OAc)_2]$ **1** ($\delta = 22.79$ ppm) and binuclear $[Zn_2\mathbf{L1}(HOAc)]$ **5** ($\delta = 21.60$ ppm) for the OAc fragments. Therefore, the synthesis of **5** in conjunction with the data for the previously reported structure (Fig. 1) thus supports that the reaction stoichiometry is indeed a decisive parameter. The observation of low to moderate yields for multinuclear **1–3** and dinuclear **5** (17–61%) is ascribed to side-product formation that is caused by *in situ* equilibration of the mono-imines **A** and **B** giving the fully condensed salphen ligands that, upon metalation, can furnish mononuclear Zn(salphen)s such as **6**.

Conclusions

In this contribution we have detailed the influence of the reaction stoichiometry on the outcome of the metalation process for various (chiral) bis-salphen scaffolds. In the case of an excess of Zn reagent, incorporation of $Zn(OAc)_2$ or $Zn(OH)_2$ salts *via* coordinative patterns that involve either bridging OAc or OH anions is observed leading to structures with the formula $[Zn_3\mathbf{L}(OAc)_2]_2$ or $[Zn_3\mathbf{L}(OH)_2]_2$ while the use of a slight deficit of Zn reagent leads to the incorporation of HOAc as previously observed giving structures generally described as $[Zn_2\mathbf{L}(HOAc)]$. This information is of high importance, since these bis-Zn(salphen) scaffolds are excellent supramolecular host systems for chirogenesis effects within the context of the determination of absolute configurations of various ditopic substrates; these ditopic substrates bind to both Zn ions and competitive binding of anionic ligands compromises the effectiveness of the host systems. Thus the present results help to understand and design new host systems that do not contain yet a competitive guest that needs to be exchanged prior to the chirogenesis process. The current focus is therefore on the design and isolation of acid- and/or salt-free host systems and results will be reported in due course.

Experimental

General comments

All reagents are commercially available and were used as received. NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. Elemental analysis was performed by the Unidád de Análisis Elemental at the University of Santiago de Compostela (Spain). Mass spectrometric analysis and X-ray diffraction studies were performed by the Research Support Area at the ICIQ. Both mono-imine reagents **A**, **B** and precursor ligand $\mathbf{L4}$-H_4 were prepared according to previously published procedures.[11,13] The aldehydes 3,3′-diformyl-2,2′-dihydroxy-1,1′-biphenyl[14] and (*S*)-2,2′-dihydroxy-[1,1′-binaphthalene]-3,3′-dialdehyde[15] were prepared as reported.

Preparation of trinuclear complex $[Zn_3\mathbf{L1}(OAc)_2]$ 1. To a solution of 3,3′-diformyl-2,2′-dihydroxy-1,1′-biphenyl (93 mg, 0.38 mmol) and the mono-imine reagent **A** (252 mg, 0.77 mmol) in $CHCl_3$ (20 mL) was added a solution of $Zn(OAc)_2\cdot 2H_2O$ (182 mg, 0.83 mmol) dissolved in MeOH–pyridine (15 mL, 2 : 1 v/v). The dark orange solution was stirred for 18 h after which it was concentrated. Addition of CH_3CN caused precipitation of an orange solid that was collected by filtration and dried (116 mg). A second fraction of the product could be obtained by cooling the mother liquor to 6 °C (60 mg). Total yield: 176 mg (0.179 mmol, 47% based on dialdehyde). Crystals suitable for X-ray diffraction were obtained from CH_3CN in the presence of *n*-hexylamine. ^1H NMR (400 MHz, [d$_6$]DMSO): $\delta = 9.00$ (s, 2H; CH=N), 8.94 (s, 2H; CH=N), 7.99 (d, $^3J_{H,H} = 7.1$ Hz, $^4J_{H,H} = 1.8$ Hz, 2H; ArH), 7.84–7.88 (m, 4H; ArH), 7.33–7.36 (m, 6H; ArH), 7.30 (d, $^4J_{H,H} = 2.5$ Hz, 2H; ArH), 7.20 (d, $^4J_{H,H} = 2.6$ Hz, 2H; ArH), 6.60 (t, $^3J_{H,H} = 7.5$ Hz, 2H; ArH), 1.81 (s, 6H; OAc), 1.46 (s, 18H; $C(CH_3)_3$), 1.27 (s, 18H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [d$_6$]acetone): $\delta = 170.62$, 163.62, 163.26, 141.23, 140.37, 140.10, 137.80, 134.95, 133.66, 130.82, 129.96, 128.76, 127.24, 127.07, 119.94, 118.66, 116.73, 116.65, 112.89, 36.15, 35.59, 31.80, 30.21, 22.79; MS (MALDI+, dctb): $m/z = 1168.4$ $(M)^+$, 982.3 $(M - Zn(OAc)_2)^+$ (calcd 982.3). Elemental analysis calcd (%) for $C_{60}H_{64}N_4O_8Zn_3\cdot 3H_2O$: C 59.10, H 5.79, N 4.59; found: C 59.05, H 5.26, N 4.49.

Preparation of chiral trinuclear complex $[Zn_3\mathbf{L2}(OAc)_2]$ 2. (*S*)-2,2′-Dihydroxy-[1,1′-binaphthalene]-3,3′-dialdehyde (51 mg, 0.15 mmol) and monoimine reagent **A** (104 mg, 0.32 mmol) were dissolved in DCM (5 mL). To this mixture was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (77 mg, 0.35 mmol) dissolved in MeOH (2.5 mL) and a few drops of NEt_3. The solution was left stirring for 6 h and then cooled to −30 °C to induce precipitation of the product. The desired compound was isolated by filtration and dried *in vacuo* to yield an orange solid (81 mg, 43% based on dialdehyde). ^1H NMR (400 MHz, [d$_6$]acetone): δ = 9.40 (s, 2H; CH═N), 8.86 (s, 2H; CH═N), 8.55 (s, 2H; ArH), 8.07 (d, $^3J_{H,H}$ = 8.1 Hz, 2H; ArH), 7.95 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; ArH), 7.86 (d, $^3J_{H,H}$ = 7.1 Hz, 2H; ArH), 7.50 (t, $^3J_{H,H}$ = 8.7 Hz, 2H; ArH), 7.45 (t, $^3J_{H,H}$ = 8.5 Hz, 2H; ArH), 7.34 (t, $^3J_{H,H}$ = 8.9 Hz, 2H; ArH), 7.22 (t, overlapping peak *J* not resolved, 2H; ArH), 7.21 (d, $^4J_{H,H}$ = 2.9 Hz, 2H; ArH), 7.09 (d, $^4J_{H,H}$ = 2.5 Hz, 2H; ArH), 7.00 (d, $^3J_{H,H}$ = 8.7 Hz, 2H; ArH), 1.53 (s, 6H; OAc), 1.23 (s, 18H; $C(CH_3)_3$), 0.71 (s, 18H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [d$_6$]acetone): δ = 171.08, 170.45, 165.27, 163.12, 158.36, 152.22, 141.57, 140.87, 140.05, 139.07, 137.42, 134.13, 129.38, 128.99, 128.92, 128.73, 128.20, 127.18, 126.07, 124.68, 123.24, 122.97, 118.51, 117.70, 115.92, 34.56, 33.39, 30.79; MS (MALDI+, dctb): *m*/*z* = 1264.3 [M]$^+$ (calcd 1264.3), 1205.3 [M − (OAc)]$^+$ (calcd 1205.3), 1080.3 [M − $Zn(OAc)_2$]$^+$ (calcd 1080.3). Elemental analysis calcd (%) for $C_{66}H_{66}N_4O_6Zn_2 \cdot Zn(OAc)_2 \cdot 1.5H_2O$: C 63.19, H 5.54, N 4.33; found: C 63.24, H 5.51, N 4.37.

Preparation of chiral trinuclear complex [Zn_3L3$(OAc)_2$] 3. (*S*)-2,2′-Dihydroxy-[1,1′-binaphthalene]-3,3′-dialdehyde (49 mg, 0.14 mmol) and mono-imine reagent **B** (79 mg, 0.29 mmol) were dissolved in DCM (5 mL). To this mixture was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (82 mg, 0.37 mmol) dissolved in MeOH (2.5 mL) and a few drops of NEt_3. The solution was left stirring for 6 h and then cooled to −30 °C to induce precipitation of the product. The desired compound was isolated by filtration and dried *in vacuo* to yield an orange solid (98 mg, 61% based on dialdehyde). ^1H NMR (500 MHz, [d$_6$]DMSO): δ = 9.28 (s, 2H; CH═N), 8.73 (s, 2H; CH═N), 8.17 (s, 2H; ArH), 7.92 (m, 2H; ArH), 7.74 (m, 4H; ArH), 7.40 (m, 4H; ArH), 7.09 (d, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.6 Hz; ArH), 6.97 (m, 8H; ArH), 6.26 (t, $^3J_{H,H}$ = 8.5 Hz; ArH), 1.81 (s, 6H; OAc), 0.91 (s, 18H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125 MHz, [d$_6$]DMSO): δ = 172.53, 165.47, 164.28, 163.94, 141.95, 141.17, 139.82, 138.33, 137.37, 134.66, 130.56, 129.36, 128.28, 127.40, 127.19, 125.21, 124.86, 123.90, 123.81, 119.85, 119.56, 117.14, 116.93, 112.22, 100.03, 34.82, 29.77, 22.79; MS (MALDI+, dctb): *m*/*z* = 1152.3 [M]$^+$ (calcd 1152.2), 1093.3 [M − (OAc)]$^+$ (calcd 1093.2), 968.3 [M − $Zn(OAc)_2$]$^+$ (calcd 968.2). Elemental analysis calcd (%) for $C_{58}H_{50}N_4O_6Zn_2 \cdot Zn(OAc)_2 \cdot H_2O$: C 61.53, H 4.65, N 4.78; found: C 61.33, H 4.91, N 4.74.

Preparation of chiral hexanuclear complex [Zn_3L4$(OH)_2$]$_2$ 4. To a suspension of ligand **C** (200 mg, 0.26 mmol) in anhydrous hexane (5 mL) was slowly added $ZnEt_2$ (0.77 mL 1 M in hexanes, 0.77 mmol) under a nitrogen atmosphere. The resulting mixture was stirred for 18 h. The precipitate that had formed was then filtered off to give an orange solid. Yield: 235 mg (0.12 mmol of Zn_6, 92% based on the ligand precursor). Crystals suitable for X-ray diffraction studies were obtained from DCM. ^1H NMR (500 MHz, CD_2Cl_2, mixture of four diastereoisomers 1 : 1 : 1 : 1 ratio): δ = −0.64 (s, 8H; OH), 0.12 (s, 8H; OH), 6.20 (m, 16H; ArH), 6.30 (t, $^3J_{H,H}$ = 7.5 Hz, 8H; ArH), 6.45 (t, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.8 Hz, 8H; ArH), 6.49 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.1 Hz, 8H; ArH), 6.54 (dd, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 2.0 Hz, 8H; ArH), 6.62 (dd, $^3J_{H,H}$ = 8.59, $^4J_{H,H}$ = 1.24 Hz, 8H; ArH), 6.70 (dd, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 1.2 Hz, 8H; ArH), 6.81 (t, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.4 Hz, 8H; ArH), 6.85 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.2 Hz, 8H; ArH), 6.92 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.7 Hz, 8H; ArH), 6.98 (dd, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.3 Hz, 8H; ArH), 7.04 (m, 32H; ArH), 7.10 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.8 Hz, 16H; ArH), 7.21 (t, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.2 Hz, 16H; ArH), 7.32 (m, 40H; ArH), 7.43 (m, 16H; ArH), 7.50 (t, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.4 Hz, 16H; ArH), 7.62 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.0 Hz, 8H; ArH), 7.70 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.3 Hz, 8H; ArH), 8.08 (s, 8H; CH═N), 8.79 (s, 8H; CH═N); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, mixture of four diastereoisomers in a 1 : 1 : 1 : 1 ratio): δ = 112.66, 115.61, 116.20, 116.31, 116.83, 117.21, 120.31, 120.46, 122.13, 122.95, 123.17, 123.69, 123.84, 124.15, 125.56, 125.85, 126.21, 126.71, 127.96, 128.04, 128.20, 128.27, 128.34, 128.39, 132.18, 132.54, 133.54, 133.86, 134.67, 134.73, 135.12, 135.81, 137.22, 137.30, 137.43, 139.31, 140.23, 140.51, 140.81, 141.20, 162.80, 164.19, 165.05, 166.40, 167.97, 171.32, 173.40, 174.63; MS (MALDI+, dctb): *m*/*z* = 1983.3 (M − 2OH)$^+$ (calcd 1983.1). Elemental analysis calcd (%) for $C_{104}H_{72}N_8O_{12}Zn_6 \cdot 7H_2O$: C 58.26, H 4.04, N 5.23; found: C 58.37, H 3.74, N 5.08.

Preparation of dinuclear complex [Zn_2L1(HOAc)] 5. To a solution of 3,3′-diformyl-2,2′-dihydroxy-1,1′-biphenyl (81.9 mg, 0.338 mmol) and the mono-imine reagent **A** (226.1 mg, 0.697 mmol) in $CHCl_3$ (20 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (141.1 mg, 0.643 mmol) dissolved in MeOH–pyridine (10 mL : 1 mL). The orange solution was stirred for 4 h after which it was concentrated. Addition of CH_3CN caused precipitation of an orange solid that was collected by filtration and dried (178.7 mg). This product was shown to be a mixture of **5** and **6** in a 1 : 1.3 ratio by ^1H NMR signal integration. Recrystallization of this mixture from warm MeOH afforded pure **5**, while subsequent fractions contained impure material. Yield: 57.1 mg (0.0548 mmol, 17% based on the Zn reagent). ^1H NMR (400 MHz, [d$_6$]DMSO): δ = 8.99 (s, 2H; CH═N), 8.94 (s, 2H; CH═N), 8.00 (d, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.7 Hz, 2H; ArH), 7.84–7.88 (m, 4H; ArH), 7.34–7.37 (m, 6H; ArH), 7.30 (d, $^4J_{H,H}$ = 2.4 Hz, 2H; ArH), 7.21 (d, $^4J_{H,H}$ = 2.4 Hz, 2H; ArH), 6.61 (t, $^3J_{H,H}$ = 7.5 Hz, 2H; ArH), 1.90 (s, 3H; OAc), 1.47 (s, 18H; $C(CH_3)_3$), 1.27 (s, 18H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [d$_6$]acetone): δ = 170.63, 163.64, 163.28, 141.25, 140.39, 140.12, 137.82, 134.98, 133.68, 130.84, 129.98, 128.80, 127.26, 127.09, 119.96, 118.68, 116.76, 116.69, 112.92, 35.62, 33.99, 31.82, 30.22, 21.60; MS (MALDI+, dctb): *m*/*z* = 982.4 (M − HOAc)$^+$ (calcd 982.3). Elemental analysis calcd (%) for $C_{58}H_{62}N_4O_6Zn_2 \cdot 4H_2O$: C 62.54, H 6.33, N 5.03; found: C 62.37, H 6.33, N 5.20.

Crystallographic studies

General: The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions immersed in perfluoropoly-ether as a protecting oil for manipulation. Data collection: Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, an FR591 rotating anode with MoKα radiation, Montel mirrors and a Kryoflex low temperature device ($T = -173$ °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint + Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008). Structure solution: SHELXTL Version 6.10 (Sheldrick, 2000)[16] was used. Structure refinement: SHELXTL-97-UNIX VERSION.

Crystal data for [Zn$_3$**L1**(OAc)$_2$] **1**·CH$_3$CN: $C_{80}H_{112}N_8O_8Zn_3$, $M_r = 1509.89$, triclinic, $P\bar{1}$, $a = 15.2147(15)$ Å, $b = 17.6284(18)$ Å, $c = 17.8255(16)$ Å, $\alpha = 112.366(3)°$, $\beta = 113.184(2)°$, $\gamma = 90.041(3)°$, $V = 4000.1(7)$ Å^3, $Z = 2$, $\rho = 1.254$ mg M^{-3}, $\mu = 0.949$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 1604$, crystal size = 0.15 × 0.06 × 0.03 mm, θ (min) = 1.27°, θ (max) = 30.68°, 15 867 reflections collected, 15 417 reflections unique ($R_{\text{int}} = 0.0139$), GoF = 1.045, $R_1 = 0.0723$ and w$R_2 = 0.1959$ [$I > 2\sigma(I)$], $R_1 = 0.1338$ and w$R_2 = 0.2403$ (all indices), min/max residual density = −0.868/1.168 [e Å^{-3}]. Note the completeness to θ (30.68°) is only 62.1%; this is due to the long time required for collecting the data which caused ice formation, and the measurement had to be interrupted. Nonetheless, the connectivity pattern is clearly established. Data collection with a long exposure time has been made to reach the maximal data resolution in order to model the disorder. Higher resolution data allow us to have a good data-to-parameter ratio (15 : 1 for the current structure). The structure has been deposited at the CCDC with reference number 871926.

Crystal data for [Zn$_3$**L4**(OH)$_2$]$_2$ **4**·5.5(ClCH$_2$CH$_2$Cl)·2.5-(CH$_2$Cl$_2$): $C_{117.5}H_{99}N_8O_{12}Cl_{16}Zn_6$, $M_r = 2774.46$, monoclinic, $C2/c$, $a = 26.743(2)$ Å, $b = 17.5255(15)$ Å, $c = 24.944(2)$ Å, $\alpha = 90°$, $\beta = 104.816(3)°$, $\gamma = 90°$, $V = 11302.2(17)$ Å^3, $Z = 4$, $\rho = 1.631$ mg M^{-3}, $\mu = 1.698$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 5632$, crystal size = 0.30 × 0.20 × 0.10 mm, θ (min) = 1.74°, θ (max) = 31.87°, 306 121 reflections collected, 19 311 reflections unique ($R_{\text{int}} = 0.0500$), GoF = 1.037, $R_1 = 0.0533$ and w$R_2 = 0.1423$ [$I > 2\sigma(I)$], $R_1 = 0.0720$ and w$R_2 = 0.1578$ (all indices), min/max residual density = −1.626/1.106 [e Å^{-3}]. Completeness to θ (31.87°) = 99.6%. The structure has been deposited at the CCDC with reference number 871927.

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