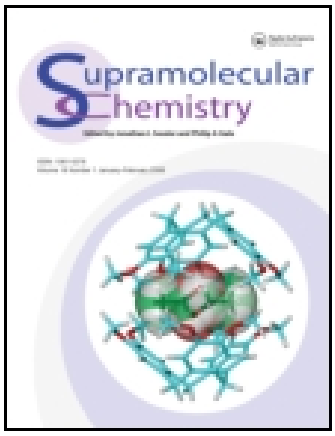


Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

Synthesis of acyclic tetrakis- and pentakis(N_2O_2) ligands for single-helical heterometallic complexes with a greater number of winding turns

Shigehisa Akine [a], Takashi Matsumoto [a], Shiho Sairenji [a] & Tatsuya Nabeshima [a]
[a] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8571, Japan
Published online: 22 Feb 2011.

To cite this article: Shigehisa Akine, Takashi Matsumoto, Shiho Sairenji & Tatsuya Nabeshima (2011) Synthesis of acyclic tetrakis- and pentakis(N_2O_2) ligands for single-helical heterometallic complexes with a greater number of winding turns, Supramolecular Chemistry, 23:01-02, 106-112, DOI: 10.1080/10610278.2010.514906

To link to this article: http://dx.doi.org/10.1080/10610278.2010.514906

Supramolecular Chemistry
Vol. 23, Nos. 1–2, January–February 2011, 106–112

Synthesis of acyclic tetrakis- and pentakis(N_2O_2) ligands for single-helical heterometallic complexes with a greater number of winding turns

Shigehisa Akine*, Takashi Matsumoto, Shiho Sairenji and Tatsuya Nabeshima*

Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

(*Received 28 May 2010; final version received 6 August 2010*)

Acyclic oligooxime ligands (H_8L^4 and $H_{10}L^5$) that have four or five N_2O_2 coordinating moieties (salamo moieties) were synthesised in order to obtain single-helical metal complexes with a greater number of winding turns. When the complexation of the tetrakis (salamo) ligand H_8L^4 with zinc(II) took place, a complicated mixture of zinc(II) complexes was formed. However, the mixture was converted to a discrete pentanuclear complex in the presence of a guest ion with a suitable size (La^{3+}, Ba^{2+}), which was evidenced by the well-resolved sharp ^{1}H NMR spectra and the mass spectra. Other ions with a smaller size (Lu^{3+}, Ca^{2+}) did not lead to such a discrete species. The ^{1}H NMR spectral feature of the pentanuclear complex [$L^4Zn_4La(OAc)_3$] is consistent with the single-helical structure in which the *n*th benzene ring approximately lies on the (n + 3)th benzene ring.

Keywords: helical structure; foldamer; metal complex; oxime; chelate ligand

1. Introduction

Helical molecules are useful molecular motifs that provide a chiral environment. Their unique structural features are of interest because of their various kinds of molecular functions, such as chiroptical responses. In particular, helical structures that are constructed from linear oligomeric compounds by non-covalent interactions (*1–3*) are useful as a platform for responsive molecules based on a reversible structural conversion (*4*). The helical structures can undergo interconversion between the right- and left-handed forms as well as between the helical and non-helical structures. These structural changes would change the physicochemical properties arising from the helical handedness. Therefore, such helical compounds are potentially useful for the development of novel functional molecules (*5*). For constructing the invertible helical structures, metal coordination (*1*), hydrogen bond (*2*), solvophobic interaction (*3*), etc. are available as the non-covalent interactions. In particular, metal coordination tends to provide relatively stable helical structures based on well-defined coordination geometries around each metal ion.

The reversibility of the structural conversion of helical metal complexes mainly depends on the intrinsic lability of the coordination bonds between the ligating moiety and the employed metal ions. Even if the direct helix inversion without bond dissociation is sterically hindered, helix inversion can take place via partial bond cleavage (or transient decomplexation) followed by conformational changes and reformation of the coordination bond. However, helical complexes with a greater number of winding turns are less likely to undergo helix inversion because their helix inversion needs more coordination bonds to be simultaneously cleaved. Thus, the extension of the chain lengths is expected to make the helical structures more stable and well defined.

We have investigated the functions of a series of single-helical oligometal complexes (*6–9*) that are obtained from acyclic oligomer ligands consisting of two or three N_2O_2 ligand (salamo (*10*, *11*)) moieties. Single-helical complexes with winding angles of 288° and 421° are obtained by the complexation of bis- or tris(salamo) ligands (H_4L^2, H_6L^3) with zinc(II) and lanthanum(III) (Scheme 1) (*7*, *8*). The extended analogues, tetrakis- and pentakis(salamo) ligands (H_8L^4, $H_{10}L^5$), are expected to form penta- and hexanuclear helical complexes, respectively, with a greater number of winding turns (Scheme 1), which may suppress the helix inversion. We now report the synthesis, structure and helix inversion behaviour of these extended helical metal complexes.

2. Results and discussion

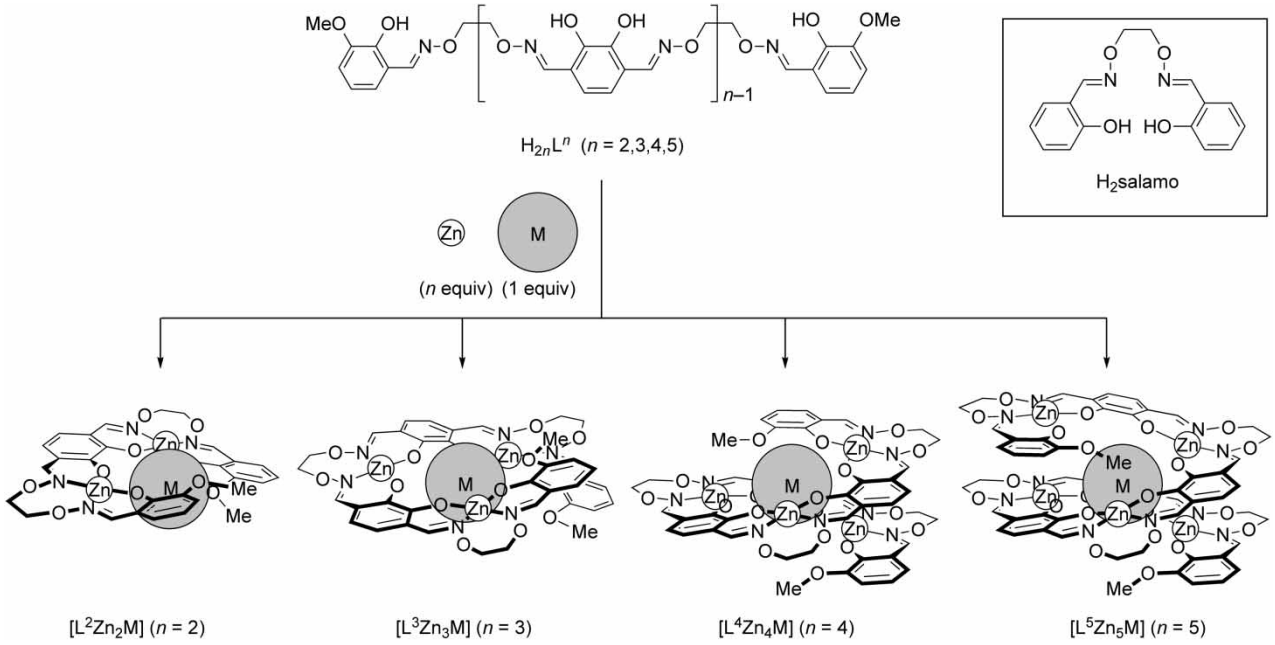
2.1 Synthesis of linear oligooxime ligands

Ligands of various chain lengths were synthesised by the sequential procedure shown in Scheme 2. Diamines **3** and **4** were synthesised by the reaction of 2,3-dihydroxybenzene-1,4-dicarbaldehyde (**1**) (*7e*) with 1,2-bis(aminooxy)-ethane (**2**) (*12*) in a 1:3 molar ratio (Scheme 2).

*Corresponding authors. Email: nabesima@chem.tsukuba.ac.jp; akine@chem.tsukuba.ac.jp

ISSN 1061-0278 print/ISSN 1029-0478 online

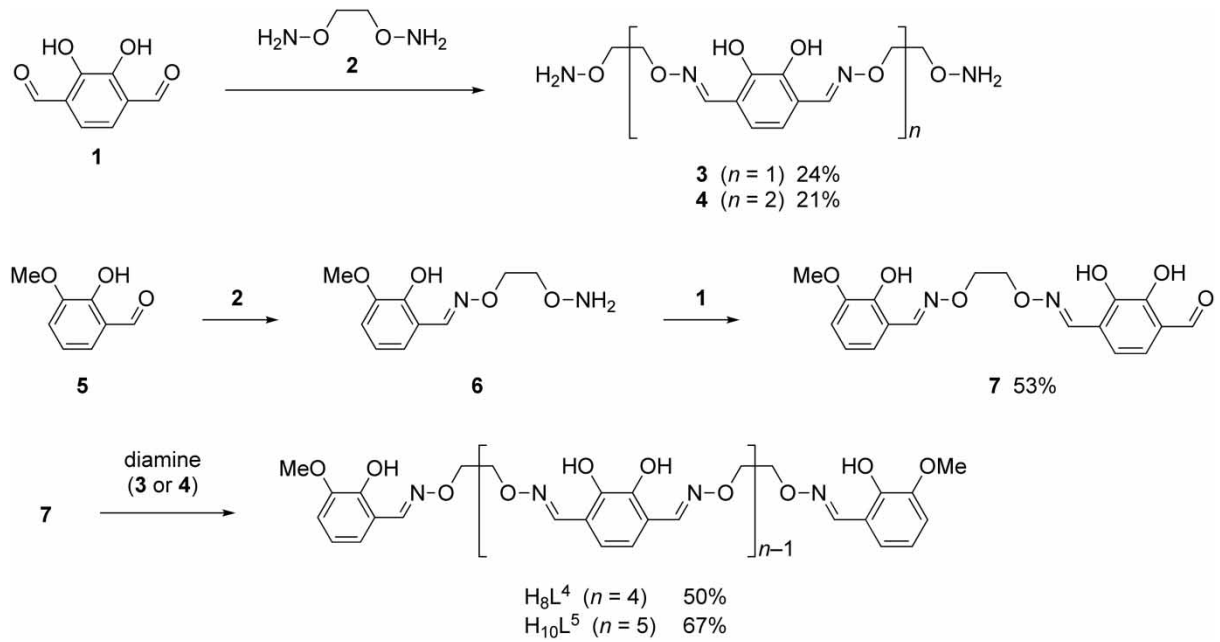
DOI: 10.1080/10610278.2010.514906
http://www.informaworld.com



Scheme 1. Formation of single-helical complexes by metalation of acyclic oligo(salamo) ligands.

The reaction mixture was separated by gel permeation chromatography (GPC) to yield the 1:2 condensation product **3** (*7k*) and 2:3 condensation product **4** in 24 and 21% yields, respectively.

The mono-coupling product **6** (*10b*), which was obtained by the condensation of 2-hydroxy-3-methoxybenzaldehyde (**5**) with diamine **2**, was treated with dialdehyde **1** to give the formyl-functionalised salamo derivative **7** (*7b*). The reaction of this aldehyde **7** with diamines **3** and **4** of different chain lengths yielded the acyclic oligo(salamo) ligands H_8L^4 and $H_{10}L^5$, respectively. The pentakis(salamo) ligand $H_{10}L^5$ was almost insoluble in chloroform and methanol. Thus, titration experiments were carried out only for the tetrakis(salamo) ligand H_8L^4.



Scheme 2. Synthesis of oligo(salamo) ligands H_8L^4 and $H_{10}L^5$.

2.2 Complexation of tetrakis(salamo) ligand H_8L^4 with zinc(II)

We have previously reported that the shorter bis(salamo) ligand H_4L^2 quantitatively forms a zinc(II) trinuclear complex upon the complexation with 3 equiv. of zinc(II) acetate (*7a*,*e*,*g*). However, the corresponding reaction of the tris(salamo) ligand H_6L^3 with zinc(II) acetate afforded a mixture of tetranuclear complexes (*7b*). In order to understand the correlation between the oligooxime chain lengths and structure of the metal complexes, we investigated the complexation of a longer analogue, tetrakis(salamo) H_8L^4, with zinc(II) acetate.

When zinc(II) acetate was added to a solution of H_8L^4, the colour of the mixture immediately changed to yellow, indicating the formation of the zinc(II) complex. In the ^{1}H NMR spectra of H_8L^4 in the presence of zinc(II) acetate (4–6 equiv.), no signals appeared for the free ligand H_8L^4, indicating complete conversion. However, the new signals were too complicated to analyse the product structure (Figure 1). In the ESI mass spectrum of a solution of H_8L^4 in the presence of 4 equiv. of zinc(II) acetate, several peaks were observed, which were assigned to hexanuclear species ($m/z = 1586.9$ for $[L^4Zn_6(OAc)_3]^+$, 764.9 for $[L^4Zn_6(OAc)_2]^{2+}$), pentanuclear species ($m/z = 1405.0$ for $[L^4Zn_5(OAc)]^+$, 672.9 for $[L^4Zn_5]^{2+}$) and tetranuclear species ($m/z = 1341.1$ for $[H_2L^4Zn_4(OAc)]^+$, 1281.0 for $[HL^4Zn_4]^+$). The spectral investigation indicated that the complexation with zinc(II) did not give a single discrete complex, but a mixture containing the hexa-, penta- and tetranuclear complexes.

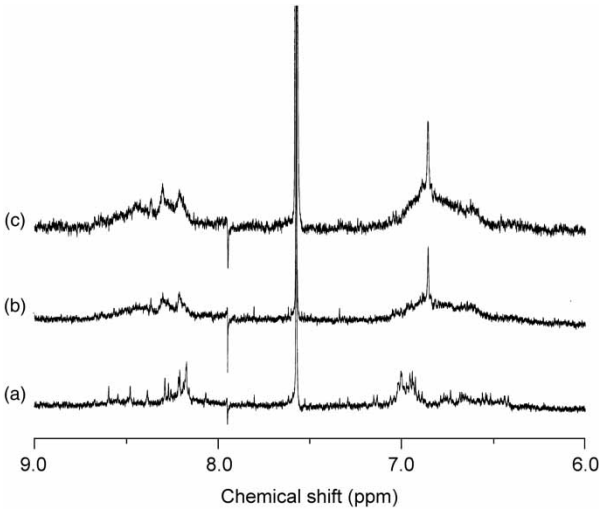


Figure 1. ^{1}H NMR spectra of H_8L^4 in the presence of zinc(II) acetate ((a) 4.0 equiv.; (b) 5.0 equiv. and (c) 6.0 equiv.) in $CDCl_3$–CD_3OD (1:1), $[H_8L^4] = 1.0$ mM, 400 MHz.

2.3 Formation of helical structure by complexation with zinc(II) and guest ion

When each N_2O_2 coordination site in ligand H_8L^4 forms a zinc(II) complex, the oligooxime ligand moiety is expected to adopt a helical conformation. Although complexation with zinc(II) afforded a complex mixture, the mixture could be converted to a single-helical complex in the presence of a guest ion that has a suitable size for the central site consisting of the eight phenoxo groups and two terminal methoxy groups as shown in Scheme 1. A similar conversion of a mixture of zinc(II) complexes to a helical Zn_3La complex is observed for the shorter ligand H_6L^3 (*7b*, *8*).

Indeed, the addition of 1 equiv. of lanthanum(III) acetate gave a ^{1}H NMR spectrum showing sharp and well-resolved signals (Figure 2(a)). This strongly indicates the formation of a single and discrete helical complex that has a symmetrical structure. The formation of the pentanuclear complex $[L^4Zn_4La]^{3+}$ was confirmed by the ESI mass spectrum, exhibiting peaks at m/z 472.9 for $[L^4Zn_4La]^{3+}$, 738.9 for $[L^4Zn_4La(OAc)]^{2+}$ and 1536.9 for $[L^4Zn_4La(OAc)_2]^+$ (Figure 3). However, the formation of this discrete species was sensitive to the anions of the source of lanthanum(III) salts. The addition of lanthanum(III) trifluoromethanesulphonate did not completely allow conversion to the tetranuclear species (Figure 2(b)). Thus, the acetate ion is necessary for the efficient formation of the pentanuclear complex $[L^4Zn_4La]^{3+}$. The observation of the species containing acetate ions ($[L^4Zn_4La(OAc)]^{2+}$ and $[L^4Zn_4La(OAc)_2]^+$) in the mass spectrum indicated the

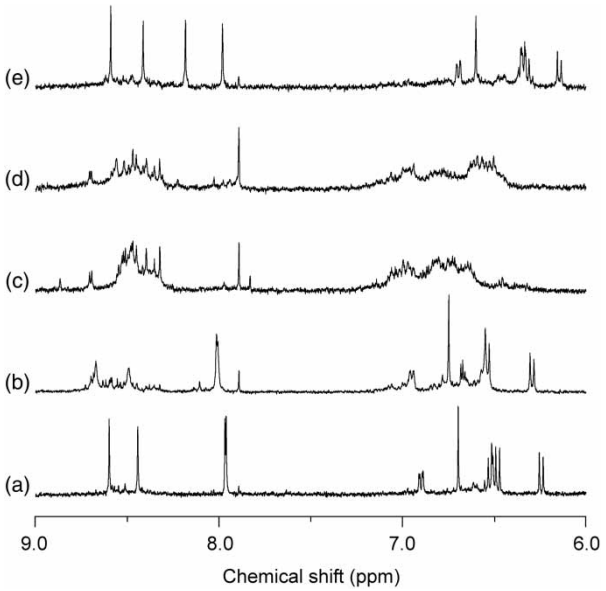


Figure 2. ^{1}H NMR spectra of H_8L^4 in the presence of $Zn(OAc)_2$ (4 equiv.) and guest metal ion ((a) $La(OAc)_3$, (b) $La(OTf)_3$, (c) $Lu(OTf)_3$, (d) $Ca(ClO_4)_2$ and (e) $Ba(ClO_4)_2$; 1 equiv.) in CD_3OD, concentration 1.0 mM, 400 MHz.

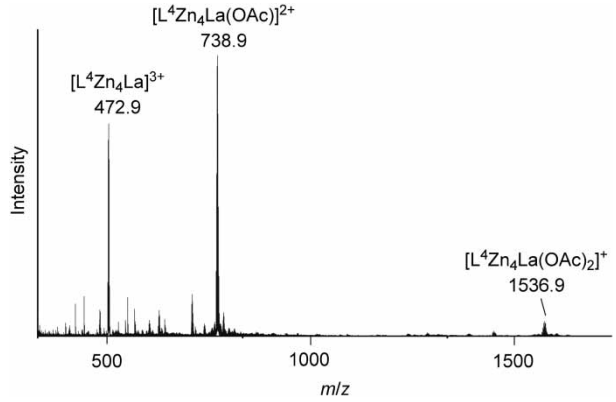


Figure 3. ESI mass spectrum of H_8L^4 in the presence of $Zn(OAc)_2$ (4 equiv.) and $La(OAc)_3$ (1 equiv.).

strong coordination of the acetate ions with the pentanuclear Zn_4La core.

The oligooxime ligand moiety forms a metal binding site that is surrounded by phenoxo oxygen atoms. The conversion process from the mixture of zinc(II) complexes to the heteronuclear Zn_4La complex is regarded as an ion recognition with concomitant release of zinc(II) ions, as seen in the shorter analogues (*7a*,*b*,*e*,*j*). We then investigated the selectivity of the ion recognition based on this metal exchange principle.

When lutetium(III) salt was used instead of lanthanum(III), the ^{1}H NMR spectrum showed a complicated pattern (Figure 2(c)). More than 10 singlets in the oxime region (7.9–8.7 ppm) were observed, indicating the formation of a complicated mixture. Since the La^{3+} and Lu^{3+} ions have the same charge number, size-fit of the ionic radius to the cavity size of the recognition site was crucial for this conversion. Among the divalent alkaline earth metals, barium ion gave a sharp and well-resolved ^{1}H NMR spectrum (Figure 2(e)), whereas calcium ion led to a complicated spectrum (Figure 2(d)). This indicates that the barium ion is more suitable for the recognition site of ligand H_8L^4 than the calcium ion.

We have reported that a shorter analogue, bis(N_2O_2) ligand H_4L^2, formed the corresponding single-helical complexes $[L^2Zn_2M]^{n+}$ upon complexation with a wide range of hard metal ions, such as the rare earth and alkaline earth metal ions (M^{n+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Y^{3+}, La^{3+}–Lu^{3+}) in the presence of zinc(II) ion. For the tetrakis(salamo) ligand, La^{3+} and Ba^{2+} fit in the central cavity, but Lu^{3+} and Ca^{2+} are not acceptable as seen in the tris(salamo) analogues (*7b*). The complexation behaviour of ligands H_6L^3 and H_8L^4 was generally similar to each other, but the longer ligand H_8L^4 with zinc(II) and La^{3+} was more affected by counter-anions of the metal source. Thus, the formation of the discrete helical structure was more sensitive to the properties of the hard metal ions when a longer ligand was used.

2.4 Structure of single-helical complexes with various winding turns in solution

Based on the investigation as well as on a previous report (*7e*, *8a*), we have demonstrated that single-helical complexes of different winding turns were formed upon complexation of the oligo(salamo) ligands of different chain lengths (H_4L^2, H_6L^3, H_8L^4) with the Zn–La or Zn–Ba combination. We then investigated the structural features of these complexes in solution in relation to the chain lengths of the oligo(salamo) ligands.

The ^{1}H NMR spectra of the heteronuclear complexes $[L^2Zn_2La(OAc)_3]$ (*7e*), $[L^3Zn_3La(OAc)_3]$ (*8a*) and $[L^4Zn_4La(OAc)_3]$ in CD_3OD are shown in Figure 4 These spectra showed oxime protons at 7.9–8.7 ppm, aromatic protons at 6.2–7.3 ppm, methylene protons at around 4.1–4.9 ppm and methoxy protons at 3.6–4.1 ppm (Table 1). There is a clear correlation between the chemical shifts of the methoxy protons and the chain lengths. While the methoxy signal of $[L^2Zn_2La(OAc)_3]$ appeared at 4.07 ppm, those of $[L^3Zn_3La(OAc)_3]$ and $[L^4Zn_4La(OAc)_3]$ were observed at 3.68 and 3.64 ppm, respectively. The upfield shifts of the longer analogues $[L^3Zn_3La(OAc)_3]$ and $[L^4Zn_4La(OAc)_3]$ indicated that the methoxy groups are shielded by the benzene rings in the other part of the chain. Similar upfield shifts were observed for some of the oxime and aromatic protons. For $[L^4Zn_4La(OAc)_3]$, oxime protons H_e, H_i and aromatic protons H_c, H_d, H_h, H_g were considerably shifted upfield. These upfield shifts suggested a structure in which the protons H_c, H_d and H_e approximately lie on the fourth benzene ring, and the protons H_g, H_h and H_i lie on the fifth benzene ring. This spectral feature is consistent with the single-helical structure in which the *n*th benzene ring approximately lies on the $(n + 3)$th benzene ring (Scheme 3).

The ^{1}H NMR spectral pattern of these helical complexes $[L^nZn_nLa(OAc)_3]$ also provides the information about the helix inversion rate. The methylene protons of the OCH_2CH_2O moieties in the shorter analogue $[L^2Zn_2La(OAc)_3]$ appeared as two broad triplets at 4.5–4.7 ppm, indicating the fast helix inversion. In contrast, the corresponding methylene protons in the longer analogues $[L^3Zn_3La(OAc)_3]$ and $[L^4Zn_4La(OAc)_3]$ appeared as several multiplets due to the diastereotopic splitting. Although the signals were not completely assigned, this spectral pattern strongly suggested the slow helix inversion on the NMR time scale.

In a manner similar to the shorter analogues, a solution of the pentakis(salamo) ligand $H_{10}L^5$ containing zinc(II) acetate (5 equiv.) and lanthanum(III) acetate (1 equiv.) was prepared. However, the spectrum was complicated, indicating the formation of several kinds of complexes. When 5 equiv. of zinc(II) was introduced at all of the N_2O_2 sites of ligand $H_{10}L^5$, 10 phenoxo groups of the resultant $[L^5Zn_5]$ moiety should surround the cavity. Probably, some of the phenoxo groups are not able to coordinate to the

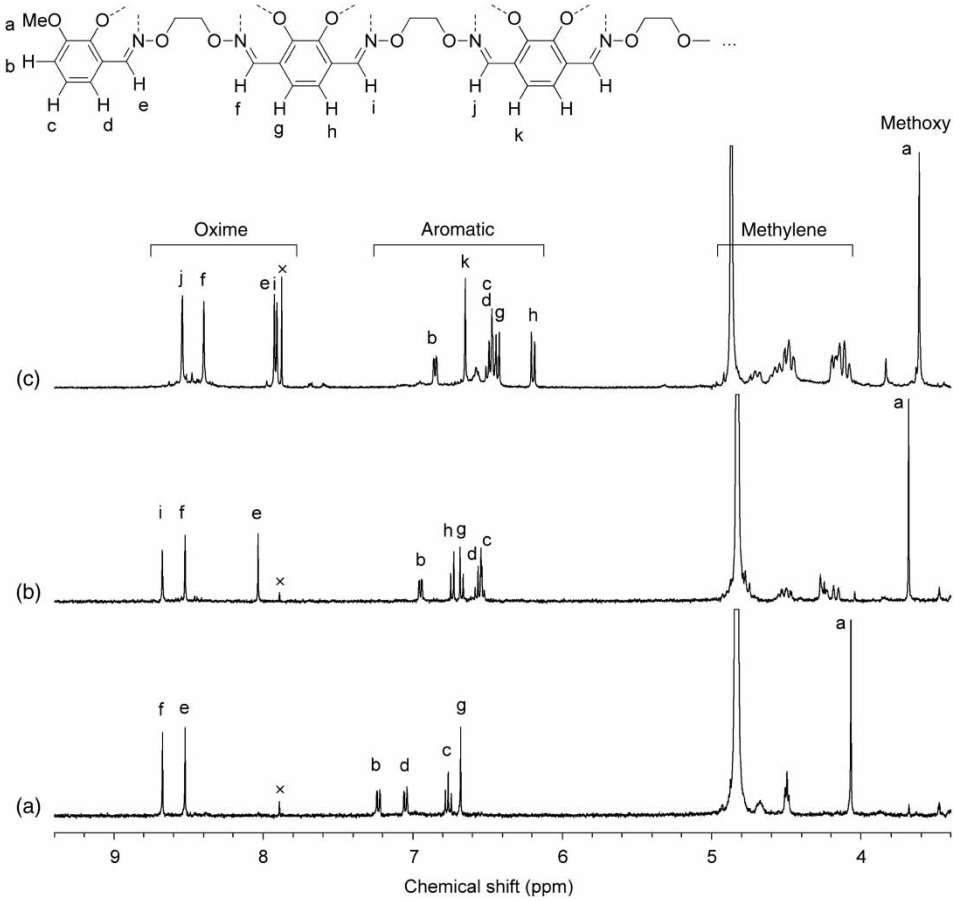


Figure 4. ^{1}H NMR spectra of (a) [$L^2Zn_2La(OAc)_3$], (b) [$L^3Zn_3La(OAc)_3$] and (c) [$L^4Zn_4La(OAc)_3$] in CD_3OD, 400 MHz.

lanthanum(III) ion, which might lead to structural variation of the complexes with a lower symmetry.

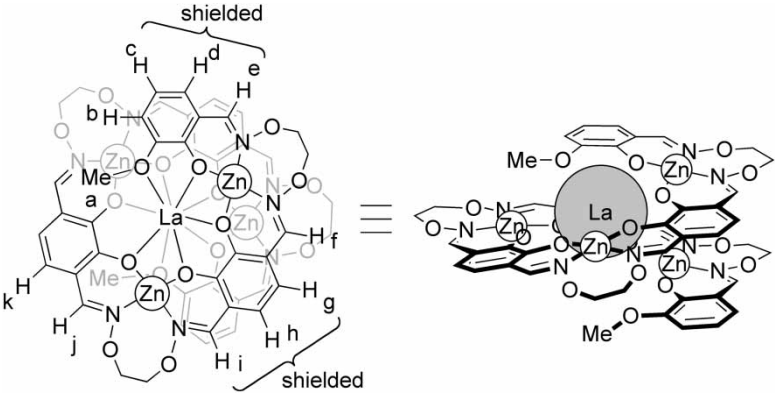
Therefore, there is a limit in the chain lengths of the oligo(salamo) ligands $H_{2n}L^n$ that form a discrete single-helical complex [$L^nZn_nLa(OAc)_3$] upon complexation with zinc(II) and lanthanum(III).

3. Conclusion

Acyclic oligooxime ligands (H_8L^4 and $H_{10}L^5$) that have four and five N_2O_2 coordinating moieties (salamo moieties) were synthesised in order to obtain single-helical metal complexes with a greater number of winding turns. When complexation of the tetrakis(salamo) ligand H_8L^4 with zinc(II) took place, a complicated mixture of zinc(II) complexes was formed. However, the mixture was converted to a discrete pentanuclear complex in the presence of a guest ion with a suitable size (La^{3+}, Ba^{2+}), which was evidenced by the well-resolved sharp ^{1}H NMR spectra and the mass spectra. Other metal ions with a smaller size (Lu^{3+}, Ca^{2+}) did not lead to such a discrete species. The ^{1}H NMR spectral feature of the pentanuclear complex [$L^4Zn_4La(OAc)_3$] is consistent with the single-helical structure in which the *n*th benzene ring approximately lies on the $(n + 3)$th benzene ring. Compared to the shorter analogues we have already reported, the formation of the helical structure from the ligand H_8L^4 in this study was more sensitive to the properties of the hard metal ions. Among the tested ions, lanthanum(III) and barium ions

Table 1. ^{1}H NMR chemical shifts of complexes [$L^nZn_nLa(OAc)_3$] ($n = 2$, 3, 4) in CD_3OD.

Complex	MeO a	ArH b	c	d	g	h	k	Oxime e	f	i	j
[$L^2Zn_2La(OAc)_3$]	4.07	7.23	6.76	7.05	6.68	–	–	8.52	8.67		
[$L^3Zn_3La(OAc)_3$]	3.68	6.94	6.53	6.56	6.67	6.74	–	8.04	8.52	8.68	
[$L^4Zn_4La(OAc)_3$]	3.64	6.88	6.52	6.49	6.46	6.23	6.68	7.96	8.43	7.94	8.57



Scheme 3. Plausible helical structure of pentanuclear complex $[L^4Zn_4La]^{3+}$.

were suitable templates for the formation of the single-helical structure from the tetrakis(salamo) ligand. The extended helical structures of the oligonuclear complexes are potentially useful for constructing various kinds of functional molecules based on the unique chiral environment containing multiple metal ions.

4. Experimental section

4.1 General procedures

All experiments were carried out in air. Commercial chloroform, methanol and ethanol were used without purification. All chemicals were of reagent grade and were used as received. GPC was performed on an LC908 (Japan Analytical Industry, Co., Ltd, Tokyo, Japan) equipped with JAIGEL 1H and 2H columns using chloroform as the eluent. Melting points were determined on a Yanaco melting point apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 or an AV400 spectrometer (400 and 100 MHz). 2D COSY and ROESY were recorded on a Bruker AVANCE 600 spectrometer (600 MHz). Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar *i* (Foster City, CA, USA) spectrometer.

4.2 Materials

2,3-Dihydroxybenzene-1,4-dicarbaldehyde (**1**) (*7e*), 1,2-bis(aminooxy)ethane (**2**) (*12*) and oxime **6** (*10b*) were synthesised according to the reported procedures.

4.3 Synthesis of diamines 3 and 4

A solution of dialdehyde **1** (213 mg, 1.28 mmol) in ethanol (14 mL) was added to a solution of 1,2-bis(aminooxy) ethane (**2**) (372 mg, 4.03 mmol) in ethanol (12 mL) at 50°C and the mixture was stirred at 50°C for 1 h. After cooling, the solution was concentrated to dryness and the crude mixture was separated by HPLC (GPC, chloroform) to yield 2:1 condensation product **3** (97.1 mg, 0.309 mmol, 24%) and 3:2 condensation product **4** (72.3 mg, 0.135 mmol, 21%) as pale yellow crystals.

4.3.1 Compound 3

Colourless crystals; m.p. 102–106°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97–3.99 (m, 4H), 4.39–4.41 (m, 4H), 5.52 (br s, 4H), 6.76 (s, 2H), 8.20 (s, 2H), 9.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.79, 73.69, 117.59, 120.58, 145.71, 150.80. Anal. calcd for $C_{12}H_{18}N_4O_6$: C, 45.86; H, 5.77; N, 17.83. Found: C, 46.05; H, 5.64; N, 17.53.

4.3.2 Compound 4

Colourless crystals; m.p. 237–241°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97–3.99 (m, 4H), 4.39–4.41 (m, 4H), 4.52 (s, 4H), 5.53 (br s, 4H), 6.75 (d, $J = 8.1$ Hz, 2H), 6.77 (d, $J = 8.1$ Hz, 2H), 8.20 (s, 2H), 8.24 (s, 2H), 9.65 (s, 2H), 9.76 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 72.83, 73.25, 73.72, 117.51, 117.69, 120.66, 120.74, 145.72, 145.74, 150.84, 151.33. Anal. calcd for $C_{22}H_{28}N_6O_{10}\cdot 0.5H_2O$: C, 48.44; H, 5.36; N, 15.41. Found: C, 48.72; H, 5.27; N, 15.21.

4.4 Synthesis of aldehyde 7

A solution of **6** (113 mg, 0.50 mmol) in ethanol (8 mL) was slowly added to a solution of dialdehyde **1** (166 mg, 1.0 mmol) in ethanol (7 mL) at 53°C and the mixture was heated for further 1 h at 53°C. The mixture was allowed to cool and filtered. The filtrate was concentrated to dryness and the residue was purified by HPLC (GPC, chloroform) to afford **7** (99.5 mg, 53%) as yellow crystals; m.p. 135–136°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 4.49–4.56 (m, 4H), 6.84–6.91 (m, 4H), 7.14 (d, $J = 8.0$ Hz, 1H), 8.26 (s, 1H), 8.28 (s, 1H), 9.70 (s, 1H), 9.72 (s, 1H), 9.92 (s, 1H), 10.94 (s, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 56.15, 73.02, 73.62, 113.52, 116.38, 119.50, 120.47, 120.80, 121.32, 122.39, 122.87, 145.96, 147.01, 148.10, 150.33, 150.81, 152.00, 196.07. Anal. calcd for $C_{18}H_{18}N_2O_7$·0.5EtOH: C, 57.43; H, 5.33; N, 7.05. Found: C, 57.82; H, 5.04; N, 6.81.

4.5 Synthesis of ligand H_8L^4

A solution of diamine **3** (7.83 mg, 0.025 mmol) in ethanol (1.5 mL) and chloroform (1 mL) was gradually added to a solution of aldehyde **7** (18.7 mg, 0.050 mmol) in chloroform (1 mL) and ethanol (2 mL) at 55–60°C. The mixture was stirred at the same temperature for 3 h and cooled to room temperature. The white precipitates were collected to give H_8L^4 (12.7 mg, 0.0123 mmol, 50%) as colourless crystals; m.p. 192–194°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H), 4.49–4.53 (m, 16H), 6.77 (s, 6H), 6.81–6.93 (m, 6H), 8.230 (s, 2H), 8.235 (s, 2H), 8.238 (s, 2H), 8.26 (s, 2H), 9.63 (s, 2H), 9.65 (s, 2H), 9.66 (s, 2H), 9.73 (s, 2H). Anal. calcd for $C_{48}H_{50}N_8O_{18}$·H_2O: C, 55.17; H, 5.02; N, 10.72. Found: C, 55.22; H, 4.76; N, 11.04.

4.6 Synthesis of ligand $H_{10}L^5$

A similar procedure starting with diamine **4** (13.4 mg, 0.025 mmol) and aldehyde **7** (18.7 mg, 0.050 mmol) gave $H_{10}L^5$ (20.9 mg, 0.0167 mmol, 67%) as colourless crystals; m.p. 208–210°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H), 4.49–4.55 (m, 20H), 6.77 (s, 8H), 6.81–6.93 (m, 6H), 8.24 (s × 4, 8H), 8.26 (s, 2H), 9.63 (s, 2H), 9.65 (s × 2, 4H), 9.66 (s, 2H), 9.73 (s, 2H). Anal. calcd for $C_{58}H_{60}N_{10}O_{22}$·H_2O: C, 54.97; H, 4.93; N, 11.05. Found: C, 54.64; H, 4.77; N, 11.25.

Acknowledgement

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

(1) (a) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; Wiley: Weinheim, 1995. (b) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997,** *97*, 2005–2062.
(2) Huc, I. *Eur. J. Org. Chem.* **2004**, 17–29.
(3) Hill, D.J.; Mio, M.J.; Prince, R.B.; Hughes, T.S.; Moore, J.S. *Chem. Rev.* **2001**, *101*, 3893–4011.
(4) (a) Berl, V.; Huc, I.; Khoury, R.G.; Krische, M.J.; Lehn, J.-M. *Nature*, **2000,** *407*, 720–723. (b) Dolain, C.; Maurizot, V.; Huc, I. *Angew. Chem., Int. Ed.* **2003,** *42*, 2738–2740. (c) Kolomiets, E.; Berl, V.; Odriozola, I.; Stadler, A.-M.; Kyritsakas, N.; Lehn, J.-M. *Chem. Commun.* **2003,** 2868–2869.
(5) (a) Miyake, H.; Yoshida, K.; Sugimoto, H.; Tsukube, H. *J. Am. Chem. Soc.* **2004,** *126*, 6524–6525. (b) Miyake, H.; Sugimoto, H.; Tamiaki, H.; Tsukube, H. *Chem. Commun.* **2005,** 4291–4293. (c) Miyake, H.; Kamon, H.; Miyahara, I.; Sugimoto, H.; Tsukube, H. *J. Am. Chem. Soc.* **2008,** *130*, 792–793. (d) Miyake, H.; Hikita, M.; Itazaki, M.; Nakazawa, H.; Sugimoto, H.; Tsukube, H. *Chem. Eur. J.* **2008,** *14*, 5393–5396.
(6) For a review, see: Akine, S.; Nabeshima, T. *Dalton Trans*. **2009,** 10395–10408.
(7) (a) Akine, S.; Taniguchi, T.; Nabeshima, T. *Angew. Chem., Int. Ed.* **2002,** *41*, 4670–4673. (b) Akine, S.; Taniguchi, T.; Saiki, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2005,** *127*, 540–541. (c) Akine, S.; Matsumoto, T.; Taniguchi, T.; Nabeshima, T. *Inorg. Chem.* **2005,** *44*, 3270–3274. (d) Akine, S.; Taniguchi, T.; Nabeshima, T. *Tetrahedron Lett.* **2006,** *47*, 8419–8422. (e) Akine, S.; Taniguchi, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2006,** *128*, 15765–15774. (f) Akine, S.; Kagiyama, S.; Nabeshima, T. *Inorg. Chem.* **2007,** *46*, 9525–9527. (g) Akine, S.; Taniguchi, T.; Nabeshima, T. *Inorg. Chem.* **2008,** *47*, 3255–3264. (h) Akine, S.; Utsuno, F.; Nabeshima, T. *IOP Conf. Ser.: Mater. Sci. Eng.* **2009,** *1*, 012009. (i) Akine, S.; Morita, Y.; Utsuno, F.; Nabeshima, T. *Inorg. Chem.* **2009,** *48*, 10670–10678. (j) Akine, S.; Kagiyama, S.; Nabeshima, T. *Inorg. Chem.* **2010,** *49*, 2141–2152. (k) Akine, S.; Akimoto, A.; Nabeshima, T. *Phosphorus, Sulfur Silicon Relat. Elem.* **2010,** *185*, 1000–1007.
(8) (a) Akine, S.; Taniguchi, T.; Matsumoto, T.; Nabeshima, T. *Chem. Commun.* **2006,** 4961–4963. (b) Akine, S.; Matsumoto, T.; Nabeshima, T. *Chem. Commun.* **2008,** 4604–4606.
(9) For related single-helical complexes, see: (a) Kawamoto, T.; Hammes, B.S.; Haggerty, B.; Yap, G.P.A.; Rheingold, A.L.; Borovik, A.S. *J. Am. Chem. Soc.* **1996,** *118*, 285–286. (b) Zhang, F.; Bai, S.; Yap, G.P.A.; Tarwade, V.; Fox, J.M. *J. Am. Chem. Soc.* **2005,** *127*, 10590–10599. (c) Dong, Z.; Karpowicz, R.J., Jr; Bai, S.; Yap, G.P.A.; Fox, J.M. *J. Am. Chem. Soc.* **2006,** *128*, 14242–14243. (d) Wiznycia, A.V.; Desper, J.; Levy, C.J. *Inorg. Chem.* **2006,** *45*, 10034–10036. (e) Dong, Z.; Yap, G.P.A.; Fox, J.M. *J. Am. Chem. Soc.* **2007,** *129*, 11850–11853.
(10) H_2salamo=1,2-bis(salicylideneaminooxy)ethane, see: (a) Akine, S.; Taniguchi, T.; Nabeshima, T. *Chem. Lett.* **2001,** 682–683. (b) Akine, S.; Taniguchi, T.; Dong, W.; Masubuchi, S.; Nabeshima, T. *J. Org. Chem.* **2005,** *70*, 1704–1711.
(11) (a) Akine, S.; Taniguchi, T.; Nabeshima, T. *Inorg. Chem.* **2004,** *43*, 6142–6144. (b) Akine, S.; Nabeshima, T. *Inorg. Chem.* **2005,** *44*, 1205–1207. (c) Akine, S.; Taniguchi, T.; Nabeshima, T. *Chem. Lett.* **2006,** *35*, 604–605. (d) Akine, S.; Dong, W.; Nabeshima, T. *Inorg. Chem.* **2006,** *45*, 4677–4684. (e) Akine, S.; Akimoto, A.; Shiga, T.; Oshio, H.; Nabeshima, T. *Inorg. Chem.* **2008,** *47*, 875–885. (f) Akine, S.; Utsuno, F.; Taniguchi, T. Nabeshima, T. *Eur. J. Inorg. Chem.* **2010,** 3143–3152.
(12) Dixon, D.W.; Weiss, R.H. *J. Org. Chem.* **1984**, *49*, 4487–4494.