Guest-dependent inversion rate of a tetranuclear single metallohelicate

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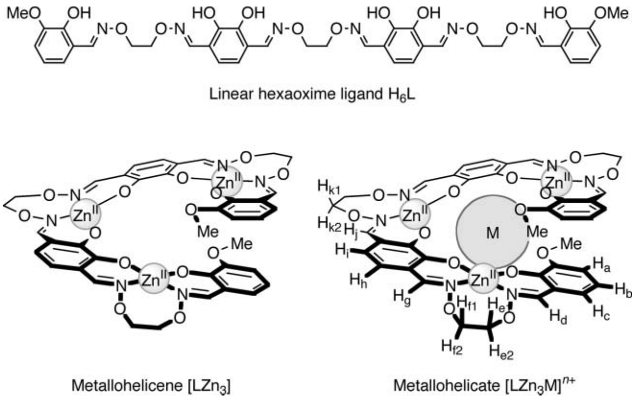
Complexation of linear hexaoxime ligand H_6L with Zn^{2+} and M^{n+} (= La^{3+}, Ba^{2+}) afforded a tetranuclear single metallohelicate $[LZn_3M]^{n+}$, whose inversion rate can be modulated by the central metal M^{n+}.

Helical molecules are versatile building blocks that form a chiral environment. In particular, helicenes have been challenging synthetic targets because of their structural interest.[1] Helicenes having a rigid and persistent structure are useful for functionalization because their interconversion between right- and left-handed helices is suppressed.[2] They have a helically delocalized π-electron system and can be utilized for interesting optical materials,[3] chiral building blocks for chiral discrimination,[4] and asymmetric catalysts.[5] Recently, helices whose helical sense is invertible by external stimuli have attracted much attention because their functions or properties depend on the helicity.[6] However, it is difficult to invert helicenes with more than one turn because of their rigidity. To solve this problem, we need a new helical scaffold other than classical helicenes. We have been investigating the synthesis of metallohosts containing labile coordination bonds, which can be utilized for the regulation of guest recognition[7] or transfer of chemical information.[8] A labile coordination bond is useful to regulate the inversion rate of helicenes *via* external stimuli. Although interesting salen-containing helical polymers or molecules have been reported so far,[9] there is no report on the inversion rate which depends on the metals in the helical molecules. We chose a linear tris(salamo) ligand H_6L[10,11] to obtain an invertible metallohelicene upon metalation of the three salamo moieties.[12] Here we report the synthesis, structure, and inversion rate of the tetranuclear single metallohelicate $[LZn_3M]^{n+}$, considered as an inclusion complex of the metallohelicene with a guest metal M^{n+}, that has a helical scaffold with more than one turn (Scheme 1). The rate of the helix inversion can be easily tuned by changing the central metal M^{n+}.

We first tried to synthesize trinuclear zinc(II) metallohelicene $[LZn_3]$ with an empty cavity by the complexation of H_6L with zinc(II) acetate (3 equiv.), but a mixture of complexes was obtained.[10] However, complexation in the presence of lanthanum(III) acetate (1 equiv.) afforded a tetranuclear complex $[LZn_3La(OAc)_3]$ in almost quantitative yield. Elemental analysis and the ESI mass spectrum (*m*/*z* 595.9 for $[LZn_3La(OAc)]^{2+}$ and *m*/*z* 1250.9 for $[LZn_3La(OAc)_2]^+$) were consistent with the structure.



Scheme 1

Single crystals of the complex suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution of $[LZn_3La(OAc)_3]$ in dichloromethane–ethanol. The X-ray crystallographic analysis revealed that three zinc atoms sit in the N_2O_2 salamo sites and have a distorted trigonal bipyramidal geometry (Fig. 1).† The lanthanum atom is in the central cavity of the molecule. All oxygen donors of the central O_8 site (six phenolates and two terminal methoxy groups) coordinate to La1. In addition, three acetate ions and an ethanol molecule coordinated to the Zn_3La metal centers. As expected, the ligand moiety forms a single helix. The winding angle of the ligand from one methoxy group to the other is defined as the sum of the seven O–M–O angles. The

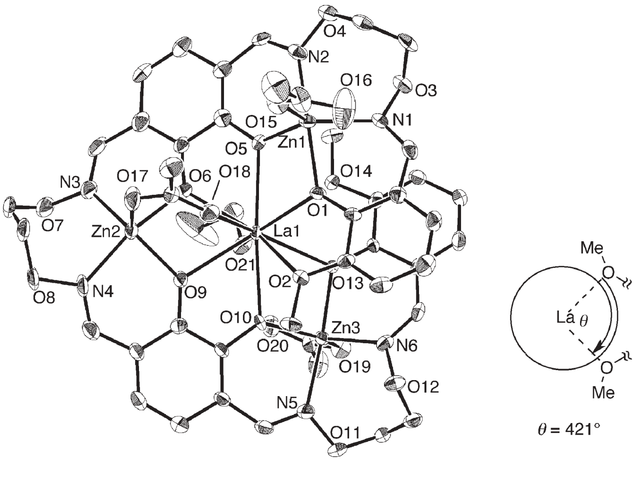


Fig. 1 X-Ray crystal structure of $[LZn_3La(OAc)_3(EtOH)]$ (50% probability level). Selected interatomic distances (Å) and angles (°); La1–O1 2.502(4), La1–O2 2.849(4), La1–O5 2.565(4), La1–O6 2.468(4), La1–O9 2.527(4), La1–O10 2.578(4), La1–O13 2.530(4), La1–O14 3.224(4), La1–O18 2.532(5), La1–O21 2.563(5), O1–La1–O2 57.15(13), O1–La1–O5 62.69(14), O5–La1–O6 62.37(14), O6–La1–O9 63.49(15), O9–La1–O10 61.08(13), O10–La1–O13 62.24(13), O13–La1–O14 52.43(12).

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angle is calculated to be 421°, which corresponds to a 1.2-turn. Both terminal salicylidene moieties of the ligand stack parallel to each other at a distance of 3.3 Å, indicative of a π–π stacking interaction (Fig. 2).

In the ^{1}H NMR spectrum of the heterotetranuclear complex $[LZn_3La]^{3+}$ in $CDCl_3$–CD_3OD (1 : 1), one singlet for the terminal methoxy proton (3.67 ppm), three singlets for oxime protons (7.86, 8.33, and 8.54 ppm), and five signals for aromatic protons were observed (Fig. 3). Only the terminal oxime proton (H_d: 7.86 ppm) shifted upfield considerably compared to the three protons of uncomplexed H_6L (8.31, 8.32, and 8.34 ppm). The upfield shift is attributed to the shielding of the other terminal aromatic ring. These spectral features are consistent with a C_2-symmetric helical structure in which the terminal salicylaldoxime moieties stack together. If the inversion of the helix takes place on the NMR timescale, salamo OCH_2CH_2O methylene protons (H_e, H_f, and H_k) must be observed as three signals. However, the spectrum exhibited six separate signals assignable to three methylene pairs of the diastereotopic protons (H_{e1}–H_{e2}, H_{f1}–H_{f2}, and H_{k1}–H_{k2}). This strongly indicates that the rate of the helix inversion is slow on the NMR timescale. It is noteworthy that these methylene protons did not coalesce even at 353 K in $CDCl_3$–CD_3OD (1 : 1, in a sealed tube).

In a similar manner, tetranuclear complex $[LZn_3Ba]^{2+}$ was also formed when H_6L was mixed with zinc(II) and barium acetates. Elemental analysis and the ESI mass spectrum (*m*/*z* 1185.9 for $[LZn_3Ba(OAc)]^+$) were consistent with the structure. The ^{1}H NMR spectrum at 293 K exhibited a spectral pattern similar to that of $[LZn_3La]^{3+}$. However, the smaller upfield shift of the terminal oxime proton (H_d: 8.12 ppm) suggests a loose helical conformation of $[LZn_3Ba]^{2+}$. It is noteworthy that the methylene protons were observed as several broad signals (Fig. 4). At lower temperatures (below 273 K), six separate signals were observable for the methylene protons as in the case of $[LZn_3La]^{3+}$, indicating that the barium complex $[LZn_3Ba]^{2+}$ has a similar helical conformation. At 353 K, the six methylene protons coalesce into three broad signals (4.34, 4.48, and 4.54 ppm) corresponding to the three methylene pairs. On the other hand, oxime, aromatic, and methoxy protons showed little change in the temperature range of 263–353 K. From these results, the coalescence of the methylene protons is ascribed to the inversion of the helix, rather than to the dissociation–complexation equilibrium between the ligand and metals.

Thus, the mobility of the metallohelicates is regulated by the central metal M^{n+}. Inversion of $[LZn_3Ba]^{2+}$ takes place faster than that of $[LZn_3La]^{3+}$ under the same conditions (Scheme 2). It has been difficult to modulate the inversion rate of classical helicenes without breaking a covalent bond. In contrast, the inversion rate of the metallohelicene moiety in $[LZn_3M]^{n+}$ can be easily tuned by replacing the simple module, a metal ion. The reason why there is a difference between the inversion rates of $[LZn_3La]^{3+}$ and $[LZn_3Ba]^{2+}$ is possibly explained by the following three factors. One is the difference in the ionic radius of the central metals; the smaller size of lanthanum leads to a tighter helix with shorter M–O bond distances and a greater winding angle. The second is the difference in charge number of the central metals; trivalent lanthanum forms stronger M–O bonds, which are more difficult to break during the inversion process. The third is the contribution of counter anions; the acetate ions fix the helical conformation of $[LZn_3La]^{3+}$ more strongly than that of $[LZn_3Ba]^{2+}$ *via* electrostatic interaction. Coordination of acetate ions to $[LZn_3La]^{3+}$ is

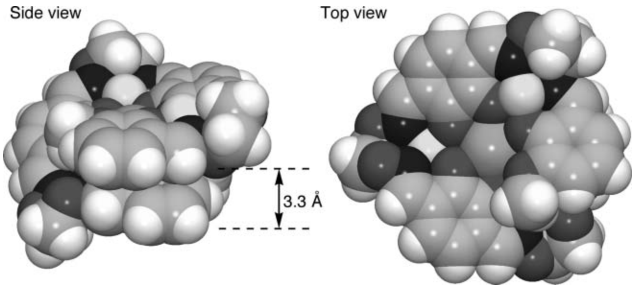


Fig. 2 Space-filling representation of the X-ray structure of $[LZn_3La]^{3+}$ showing a helical conformation.

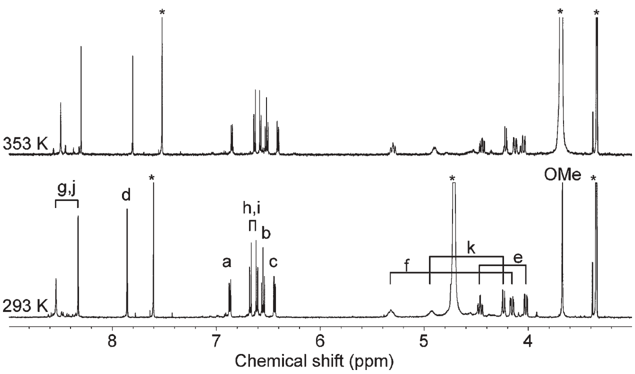


Fig. 3 ^{1}H NMR spectra (600 MHz) of $[LZn_3La]^{3+}$ in $CDCl_3$–CD_3OD (1 : 1) at 293 K and 353 K using tetramethylsilane as an internal standard. Assignments were based on 2D COSY and ROESY spectra. Solvent signals are indicated with asterisks. See Scheme 1 for atom labelling.

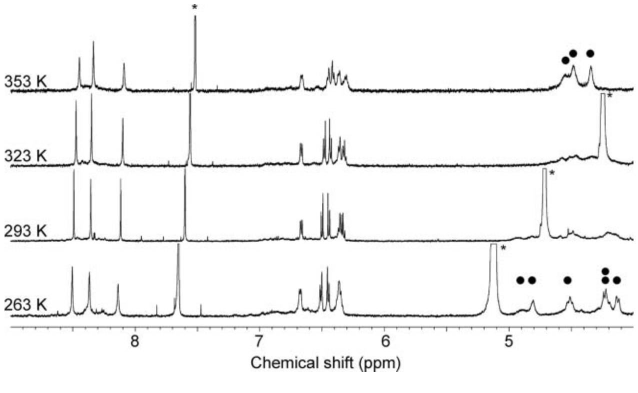
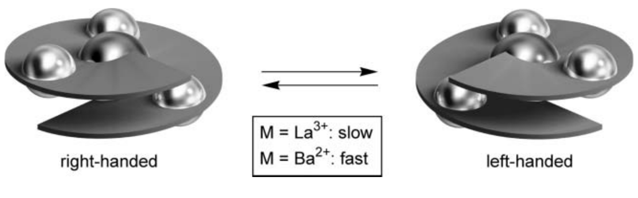


Fig. 4 ^{1}H NMR spectra (600 MHz) of $[LZn_3Ba]^{2+}$ in $CDCl_3$–CD_3OD (1 : 1) at 263–353 K using tetramethylsilane as an internal standard. Solvent signals are indicated with asterisks. Filled circles denote methylene protons H_e, H_f, and H_k.



Scheme 2

supported by considerable downfield shift of methylene protons (5.32 ppm for one of H_f and 4.92 ppm for one of H_k), indicative of C–H···O interaction to the acetate oxygen atom.[13]

The metal-containing helical strand in this work would be a useful building block for a nanocoil or molecular recognition unit responding to external stimuli. Further investigation on the extension of the metalated strand as a conducting polymer and application to discrimination of chiral molecules is in progress.

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Notes and references

† Crystal data for $[LZn_3La(OAc)_3(EtOH)]\cdot H_2O$: $C_{46}H_{51}LaN_6O_{22}Zn_3$ (1374.95), orange crystal (0.15 × 0.08 × 0.04 mm^3), triclinic, $P\bar{1}$, a = 8.7509(11), b = 16.449(2), c = 18.610(2) Å, α = 88.055(2), β = 83.540(2), γ = 74.640(2)°, V = 2566.7(5) Å^3, Z = 2, μ(Mo-K$_\alpha$) = 2.289 mm^{-1}, ρ_{calcd} = 1.779 g cm^{-3}, F(000) = 1384, 12 208 reflections measured, 8832 unique (R_{int} = 0.0363). Intensity data were measured at 90 K on a Bruker AXS APEX II CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (0.71073 Å). The structure was solved by Patterson methods (DIFDIF-99)[14] and refined by full-matrix least squares on F^2 using SHELXL 97.[15] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included at idealized positions refined by use of the riding models. Refinement converged with GOF = 1.031, $R1$ = 0.0424 ($I > 2\sigma(I)$), $wR2$ = 0.1108 (all data) for 722 parameters. CCDC 616056. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610641b

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