

## One-pot diastereoselective assembly of helicates based on a chiral salen scaffold



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### ABSTRACT

The one-pot reaction of (1*S*,2*S*)-(+)–1,2-diaminocyclohexane, 3-*tert*-butyl-2-hydroxybenzaldehyde and Zn(OAc)<sub>2</sub>·1.5H<sub>2</sub>O in methanol under reflux gives the diastereoselective formation of the first zinc(II)–salen double helicate, *P*-(*S*,*S*)-**1**, which adopts a right-handed helicity. The stereochemistry of the helicates can be readily tuned through varying the chiral diamine backbone.

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Asymmetric synthesis of coordination complexes is an important theme in inorganic and coordination chemistry and is attracting continuous attention from inorganic chemists, due to its promising opportunities for applications in catalysis, materials science and life sciences [1–6]. The control of metal-centered stereochemistry by chiral auxiliaries which lead to diastereoselective coordination complexes is a popular choice in this field, and via the appropriate choice of enantiopure ligand complexes with stereogenic metal centers can be prepared with excellent diastereoselectivity [7–9]. Researchers have been able to control the configuration of fascinating metal helices including mononuclear, dinuclear, trinuclear and cyclic helicates by using multitopic ligands containing two or more metal-binding domains [10,11]. The stereoselective self-assembly of helicates based on bis-pyridine type of ligands (the “chiragen” family [9]) has been extensively investigated by von Zelewsky and others, where the chiral auxiliaries are based on units derived from naturally occurring terpenes [9,12–16].

Salen is a classic bis-Schiff base type ligand containing a N<sub>2</sub>O<sub>2</sub> binding region which has proven the basis for an important class of building blocks for the self-assembly of helicates upon coordination with metal ions [17]. However, the stereoselective synthesis of salen-based helicates remains largely unexplored [18–20]. Zinc(II)–salen complexes are important candidates for catalysis and photo-/electro-luminescence materials [21], and such complexes with helical structures are rarely characterized by X-ray crystallography [18,19,22]. It was observed in the literature that many zinc(II)–salen complexes tended to form molecular aggregates through a  $\mu_2$ -O-bridging mode [23–25]. Indeed,

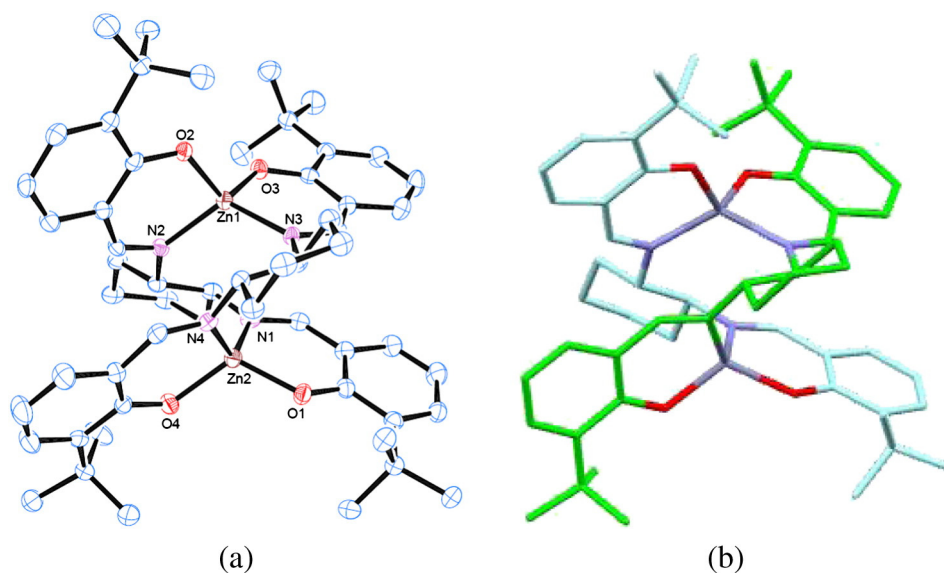
Zn(salphen) structures usually consist of dimers or oligomers through  $\mu_2$ -phenoxo (Zn–O) bridging [26].

A decade ago, Kanesato et al. isolated and crystallographically characterized the first zinc(II)–salen dinuclear double stranded helicate [27]. Recently, a triple stranded cyclic helicate of zinc(II)–salen has been structurally characterized [28]. Levy and coworkers reported the diastereoselective synthesis of mononuclear mono-stranded zinc(II)–salen complexes based on chiral salen ligands with benz[*a*]anthryl or phenanthryl sidearms, which are required for inducing helicity to the complexes [18–20]. However, chiral double stranded helicates of zinc(II)–salen are extremely rare. To the best of our knowledge, only one chiral mononuclear double helical zinc(II) complexes based on a semi-salen ligand has been reported and in that example the zinc center adopts an octahedral coordination geometry [29]. Double stranded helicates of dinuclear zinc(II)–salen with tetra-coordinate zinc center are unprecedented thus far. Herein, we report the first diastereoselective self-assembly of dinuclear zinc(II)–salen double stranded helicates through a simple one-pot synthetic protocol. In this study, we utilized a simple chiral auxiliary, enantiopure 1,2-diaminocyclohexane to control the chirality of metal–salen helicates.

One-pot reaction of the mixture of (1*S*,2*S*)-(+)–1,2-diaminocyclohexane, 3-*tert*-butyl-2-hydroxybenzaldehyde (2 equivalents) and hydrous Zn(OAc)<sub>2</sub> in CH<sub>3</sub>OH under reflux overnight afforded (*S*,*S*)-**1** as a yellow solid in high yield (89%). Characterization by UV–Vis, IR and NMR spectroscopies and elemental analysis is given in the reference [30]. (*S*,*S*)-**1** is modestly soluble in organic solvents such as dichloromethane, chloroform or acetonitrile, which allows good quality single-crystals to be obtained by solvent diffusion methods. For example, slow vapor diffusion of diethyl ether into a chloroform solution of (*S*,*S*)-**1** resulted in yellow single crystals suitable for single-crystal X-ray

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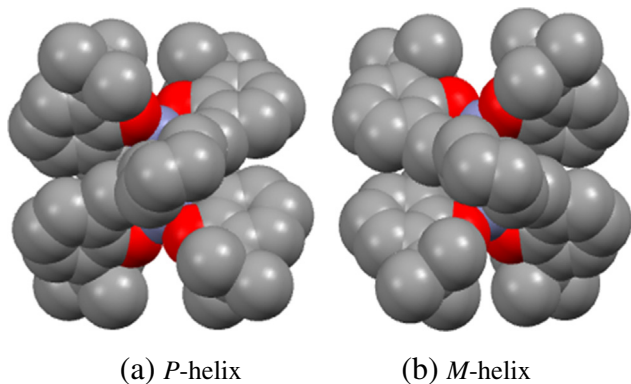


**Fig. 1.** (a) The ORTEP structure of *P*-(*S,S*)-**1** in the asymmetric unit with thermal ellipsoids at 30% probability level and (b) a wireframe view of the structure with two ligand frames in different colors. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–O2 = 1.918(2), Zn1–O3 = 1.912(3), Zn1–N2 = 2.016(3), Zn1–N3 = 2.006(3), Zn2–O1 = 1.902(3), Zn2–O4 = 1.926(3), Zn2–N1 = 2.013(3), Zn2–N4 = 2.006(3); O2–Zn1–O3 = 117.55(12), O2–Zn1–N2 = 96.13(12), O3–Zn1–N2 = 113.19(12), O2–Zn1–N3 = 114.35(12), O3–Zn1–N3 = 98.01(12), N2–Zn1–N3 = 118.97(13), O1–Zn2–O4 = 117.28(13), O1–Zn2–N1 = 97.02(13), O4–Zn2–N1 = 109.81(13), O1–Zn2–N4 = 111.01(13), O4–Zn2–N4 = 97.33(12), and N1–Zn2–N4 = 125.86(13). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

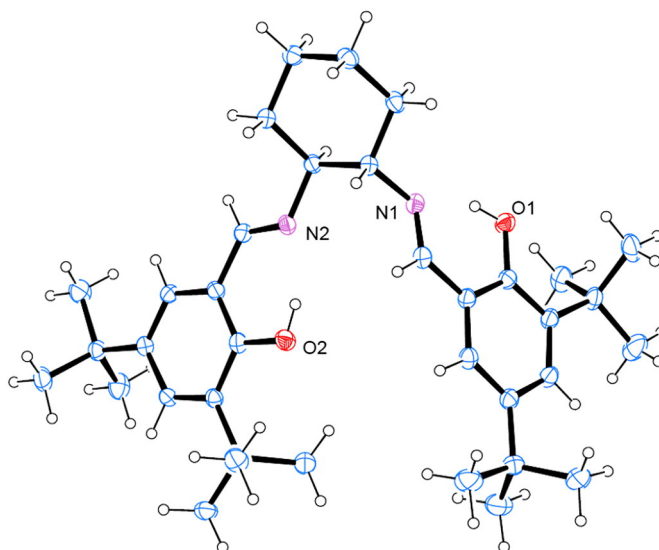
diffraction. The X-ray diffraction analysis revealed that the compound crystallized in a chiral space group  $P2_12_12_1$  [31]. The structure of a dinuclear 2:2 zinc(II) complex is shown in Fig. 1. Interestingly, the complex adopts a double-stranded helical structure, instead of the commonly observed  $\mu_2$ -O-bridging zinc complex [24,25]. One independent molecule with the right-handed *P*-helicity was revealed in the asymmetric unit and X-ray analysis on several sets of data collected from randomly selected crystals showed that those are all identical to *P*-(*S,S*)-**1**. The method for assignment of the helical chirality (*P* or *M*) has been discussed in detail elsewhere [19,32]. The optical rotation of the bulk sample of *P*-(*S,S*)-**1** in  $\text{CH}_2\text{Cl}_2$  ( $c = 1.0$ ) was estimated to be  $889.2^\circ$ . In the structure of *P*-(*S,S*)-**1** each zinc ion is bound to the  $\text{N}_2\text{O}_2$  group from two ligands, leading to distorted tetrahedral geometries on two non-equivalent zinc centers. The four Zn–O bond lengths are in the range of 1.902(3)–1.926(3) Å, while all the Zn–N bond lengths are between 2.006(3) and 2.016(3) Å, very close to the bond lengths in related zinc(II)–salen complexes [18–29]. The zinc ions are crystallographically independent and are separated by a distance of 3.844 Å, slightly longer than the achiral analog [27]. This is, however, still quite short Zn–Zn separation that leads to off-set intramolecular  $\pi$ -stacking interactions between  $\pi$ -

conjugated imines and phenyl rings, and the shortest inter-atomic distance is 3.237 Å (Fig. 2a). The intramolecular  $\pi$ -stacking is likely responsible for the bathochromic shift of fluorescence emission of *P*-(*S,S*)-**1** ( $\lambda_{\text{abs}} = 402$  nm and  $\lambda_{\text{em}} = 465$  nm in acetonitrile), in contrast to that of a mononuclear zinc(II)–salen without intramolecular  $\pi$ -stacking [27].

Single-crystals of (*S,S*)-**1** were also obtained by slow diffusion of hexane into a dichloromethane solution, while in this case yellow block-like crystals were observed. An X-ray structural determination revealed the formulation of the compound to be *P*-(*S,S*)-**1**·(hexane), which has almost identical molecular structure to *P*-(*S,S*)-**1**, except that one hexane molecule exists in each asymmetric unit in the crystal [31]. As a consequence, remarkably different molecular packing was observed in *P*-(*S,S*)-**1**·(hexane), that can be considered to be a pseudopolymorph or solvate polymorph of *P*-(*S,S*)-**1** (see Supplementary materials).



**Fig. 2.** Space-filling representations of crystal structures of helicates, *P*-(*S,S*)-**1** (a) and *M*-(*R,R*)-**1** (b).



**Fig. 3.** The ORTEP structure of **2** in the asymmetric unit with thermal ellipsoids at 30% probability level.

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