

## Synthesis and X-ray Structure of Zn(II) Complex of *N,N'*-Bis(2-fluorobenzyl)-(*R,R*)-1,2-diaminocyclohexane and Application to Nitroaldol Reaction

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Chiral ligands possessing  $C_2$  symmetry derived from (*R,R*)-1,2-diaminocyclohexane are particularly attractive auxiliaries to serve as powerful stereodirecting reagents or ligands in asymmetric synthesis, as chiral stationary phases in chromatographic separation and molecular recognition, and as chelating agents for many metals.<sup>1</sup> *Trans*-1,2-diaminocyclohexane is commercially available at relatively low cost today. It is easily resolved in aqueous medium using *L*- or *D*-tartaric acid to obtain the (*R,R*)-1,2 or the (*S,S*)-1,2-enantiomer respectively in enantiopure forms.<sup>2</sup> Beside outstanding chiral 1,2-diaminocyclohexane derivatives were synthesized and used as chiral ligands effectively in asymmetric synthesis such as chiral diimines,<sup>3</sup> chiral salens,<sup>4</sup>  $\beta$ -amino alcohols,<sup>5</sup> tetradentate chiral Schiff base ligands,<sup>6</sup> recently the synthesis and application of chiral amines including in *N*-monosubstituted;<sup>7</sup> *N,N'*-disubstituted;<sup>8</sup> *N,N'*-trisubstituted and *N,N'*-tetrasubstituted<sup>9</sup> have great progress. Some chiral 1,2-diaminocyclohexane derivatives of novel chiral  $N_4S_2$ - and  $N_4S_3$ -donor macrocyclic ligands,<sup>10</sup> chiral diamino-oligothiophenes (DATs)<sup>11</sup> were used for very good results in asymmetric nitroaldol (Henry) reaction.

The studies for the compounds of chiral *N,N'*-disubstituted  $C_2$  symmetric diamines derived from chiral 1,2-diaminocyclohexane with transition metals of Pd, Ni, Si, Rh<sup>12</sup> revealed the interesting results in their X-ray structures and catalytic capacity. Among them, chiral compounds of Ni and Si were very impressive chiral catalysts for enantioselective Michael additions and asymmetric aldehyde crotylation reaction, respectively. In the previous work,<sup>13</sup> we reported a chiral Zn complex of *N,N'*-bis(4-methoxybenzyl)-(*R,R*)-1,2-diaminocyclohexane applied for asymmetric reduction of acetophenone with promising results. In catalytic asymmetric systems, small changes in the donating ability of the ligand or the size of its substituents can have a dramatic effect on the catalyst efficiency and enantioselectivity.<sup>14</sup> In the attempts to synthesize unexpensive, effective chiral ligands and chiral Lewis acid complexes as enantioselective catalysts, herein we report the synthesis of a chiral 1,2-diaminocyclohexane derivative as a bidentate ligand of *N,N'*-bis(2-fluorobenzyl)-(*R,R*)-1,2-diaminocyclohexane, its complex with  $ZnCl_2$ , X-ray structure of the complex and its catalytic capacity towards asymmetric nitroaldol reactions.

### Experimental

**General information.** All reagents are of the reagent

grade and solvents were used as received from commercial supplies. Pure (*R,R*)-1,2-diaminonium cyclohexane mono-*L*-tartrate salt was easily prepared by the reported method.<sup>2(a)</sup> <sup>1</sup>H-NMR spectra were recorded on a Bruker advance digital 400 (400 Hz)-NMR Spectrometer at ambient temperature and chemical shifts were referenced to tetramethylsilane as internal standard and are reported in ppm. HPLC with an OD-H column was used for measurement of enantiomeric excesses (ee). Optical rotation was measured by using JASCO polarimeter. Elemental analyses were determined by using EA 1108-Elemental Analyzer at the Chemical Analysis Laboratory of the Center for Scientific Instruments of Kyungpook National University.

**Preparation of *N,N'*-bis(2-fluorobenzyl)-(*R,R*)-1,2-diaminocyclohexane, *f-L*.** A mixture of (*R,R*)-1,2-diaminonium cyclohexane mono-*L*-tartrate (4.0 g, 15.1 mmol) and  $Na_2CO_3$  (3.3 g, 30.8 mmol) in  $CH_2Cl_2$  (20 mL) and distilled water (15 mL) was stirred for 1 h. After the mixture turned to clear solutions, 2-fluorobenzaldehyde (3.3 mL, 30.6 mmol) was added and the new mixture was stirred for a day and then separated. The organic layer was dried over anhydrous  $MgSO_4$  and the solvent was removed under reduced pressure to obtain a yellowish solid product (4.6 g, 93%). To a solution of the yellow solid in methanol,  $NaBH_4$  (1.1 g, 29.4 mmol) was slowly added until to get a colorless solution. The solution was then stirred for several hours at room temperature and methanol was removed by evaporation. The residue was dissolved in 25 mL distilled water and the organic product was extracted by  $CH_2Cl_2$  and dried over anhydrous  $MgSO_4$ . Colorless oil was obtained after removing the solvent and purified by column chromatography (4.4 g, 94%). *Anal.* Calcd. for  $C_{20}H_{24}F_2N_2$ : C, 72.70; H, 7.32; N, 8.48. Found: C, 72.50; H, 7.36; N, 8.38%. <sup>1</sup>H-NMR (400 Hz,  $CDCl_3$ )  $\delta$  7.27 (m, 2H, Ph), 7.12 (m, 2H, Ph), 7.01 (m, 2H, Ph), 6.93 (m, 2H, Ph), 3.75 (dd, 4H,  $CH_2$ ), 2.16 (m, 2H, CHA), 2.07 (m, 2H, CHA), 1.83 (s, 2H, NH), 1.64 (m, 2H, CHA), 1.14 (m, 2H, CHA), 0.98 (m, 2H, CHA).

**Preparation of (*f-L*) $ZnCl_2$ .** A solution of *f-L* (1.01 g, 3.06 mmol) in ethanol (5 mL) was added dropwise to a solution of  $ZnCl_2$  (0.42 g, 3.08 mmol) in ethanol (10 mL). The mixture was stirred overnight at ambient temperature. The solvent was removed to yield white solid product. The white product was crystallized from methanol solution to form colorless crystals (1.22 g, 85%). *Anal.* Calcd. for  $C_{20}H_{24}Cl_2F_2N_2Zn$ : C, 51.47; H, 5.18; N, 6.00. Found: C, 51.42; H, 5.20; N, 6.10%. <sup>1</sup>H-NMR (400 Hz,  $CD_3CN$ )  $\delta$  7.70 (m, 2H,

**Table 1.** Crystal data and structure refinement for Zn(*f-L*)Cl<sub>2</sub>

Empirical formula	C <sub>20</sub> H <sub>24</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>2</sub> Zn
Formula weight	466.68
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system (Space group)	Orthorhombic (P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> )
Unit cell dimensions	
a	6.1915(4) Å,
b	11.1212(5) Å,
c	31.121(2) Å
Volume	2142.9(2) Å <sup>3</sup>
Z	4
Density (calculated)	1.447 Mg/m <sup>3</sup>
Absorption coefficient	1.419 mm <sup>-1</sup>
F(000)	960
θ range for data collection	1.94 to 25.47°
Index ranges	0 ≤ h ≤ 7; 0 ≤ k ≤ 13; 0 ≤ l ≤ 37
Reflections collected	2413
Independent reflections	2329 [R(int) = 0.0075]
Reflections observed (> 2σ)	2016
Data Completeness	1.000
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2329 / 0 / 161
Goodness-of-fit on F <sup>2</sup>	1.121
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.039, wR <sub>2</sub> = 0.112
R indices (all data)	R <sub>1</sub> = 0.051, wR <sub>2</sub> = 0.116
Absolute structure parameter	-0.02(2)
Largest diff. peak and hole	0.768 and -0.405 e. Å <sup>-3</sup>

Ph), 7.39 (m, 2H, Ph), 7.17 (m, 4H, Ph), 4.26 (d, 2H, CH<sub>2</sub>), 3.86 (t, 2H, CH<sub>2</sub>), 2.96 (m, 2H, CHA), 2.64 (s, 2H, NH), 2.51 (m, 2H, CHA), 1.84 (m, 2H, CHA), 1.32 (m, 4H, CHA).

**Crystal structure analysis.** A colorless single crystal suitable for X-ray analysis was sealed in a thin walled glass capillary and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Unit cell dimensions with estimated standard deviations were determined by least-squares using 25 well-centered reflections in the range of 10–13°. A total of 2413 reflections were collected using the 2θ ω scan mode. The intensity data were corrected for Lorentz-polarization effect. Crystal data and structure refinement for the complex are listed in Table 1. Data reduction was carried out using an XCAD program package and empirical absorption corrections with ABSCAL program were applied based on ψ scans.<sup>15</sup> The structure in P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> for the complex was determined by direct methods and refined by full-matrix least-squares using SHELXS-97 and SHELXL-97 program packages.<sup>16</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained by riding models. The final cycle of the refinement yielded R<sub>1</sub> = 0.039 and wR<sub>2</sub> = 0.112. Selected bond lengths and bond angles are given in Table 2.

**Catalytic nitroaldol reaction.** Reactions were carried out at low temperature (-10 °C). 10% equivalent of Zn(*f-L*)Cl<sub>2</sub> was added in 25 mL methanol and stirred. Then 3% equivalent of diisopropylethylamine or triethylamine was

**Table 2.** Selected bond lengths (Å) and angles (°) for Zn(*f-L*)Cl<sub>2</sub>

Bond lengths			
Zn-N(1)	2.056(4)	Zn-N(2)	2.095(4)
Zn-Cl(1)	2.182 (2)	Zn-Cl(2)	2.234 (2)
N(1)-C(7)	1.494(6)	N(1)-C(8)	1.498(6)
N(2)-C(14)	1.483(7)	N(2)-C(13)	1.488(6)
C(8)-C(13)	1.528(6)		
F(1)-C(5)	1.323(5)	F(2)-C(20)	1.289(5)
Bond angles			
N(1)-Zn-N(2)	86.2 (2)	N(1)-Zn-Cl(1)	120.9(1)
N(2)-Zn-Cl(1)	112.6(1)	N(1)-Zn-Cl(2)	107.0(1)
N(2)-Zn-Cl(2)	104.8 (1)	Cl(1)-Zn-Cl(2)	119.52(7)
C(7)-N(1)-C(8)	112.9(4)	C(7)-N(1)-Zn	113.4(3)
C(8)-N(1)-Zn	104.8(3)	C(14)-N(2)-C(13)	114.4(4)
C(14)-N(2)-Zn	111.0(3)	C(13)-N(2)-Zn	107.4(3)
N(1)-C(7)-C(6)	111.6(4),	N(1)-C(8)-C(9)	114.0(4)
N(1)-C(8)-C(13)	110.5(4),	N(2)-C(13)-C(8)	112.1(4),
N(2)-C(13)-C(12)	113.6(4)	N(2)-C(14)-C(15)	115.6(4)
F(1)-C(5)-C(6)	119.4(3)	F(1)-C(5)-C(4)	120.5(3)
F(2)-C(20)-C(15)	120.7(3)	F(2)-C(20)-C(19)	119.3(3)

added to the mixture of 1.1 mL nitromethane (2 equiv.) and 1.0 mL benzaldehyde. Reactions were monitored by TLC. After stirring for a week, reaction was quenched with 1 mL of 1 N HCl solution and then evaporated. The mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub> (3 times × 20 mL) and dried with anhydrous MgSO<sub>4</sub>, then filtered and the solvent was removed by evaporation. The crude product was purified by column chromatography to afford 1-phenyl-2-nitroethanol. <sup>1</sup>H-NMR (400 Hz, CDCl<sub>3</sub>): δ 7.45–7.31 (m, 5H, Ph); δ 5.43–5.38 (m, 1H, CH); δ 4.60–4.43 (dd, 2H, CH<sub>2</sub>); δ 2.96 (b, 1H, OH).

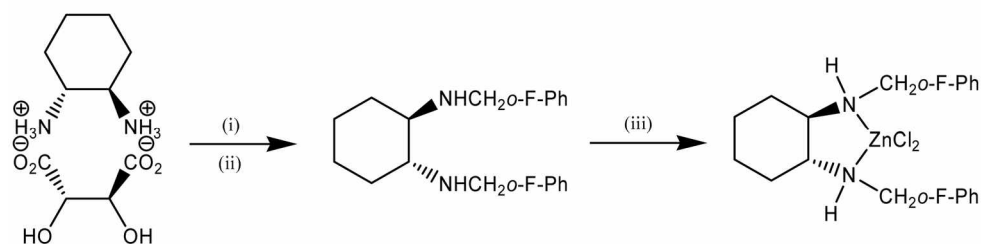
E<sub>e</sub> was determined by HPLC with a Chiralcel OD-H column at 20 °C, 15% isopropyl alcohol in hexane, flow rate 0.5 mL/min, R major enantiomer t<sub>r</sub> = 18.7 min, S minor enantiomer t<sub>r</sub> = 22.1 min. [α]<sub>D</sub> = -9.9 ~ -10.7° (c = 1, CH<sub>2</sub>Cl<sub>2</sub>, at 25 °C).

## Results and Discussion

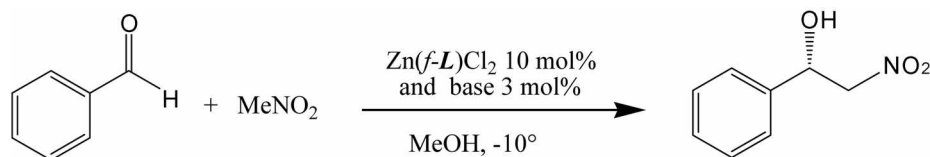
**Preparation and chemical properties.** We used stable (*R,R*)-1,2-diaminocyclohexane mono-(+)-tartrate salt to regenerate free (*R,R*)-1,2-diaminocyclohexane and to form diimine derivative directly. Then the diimine derivative received was reduced by using NaBH<sub>4</sub> to obtain the desired ligand. This chiral amine ligand was readily used for Zn(*f-L*)Cl<sub>2</sub> (Scheme 1).

The ligand is easily dissolved in polar organic solvents such as ethanol, methylene chloride and diethyl ether. The reaction of ZnCl<sub>2</sub> with *f-L* in ethanol afforded the Zn(II) complex. It is readily soluble in polar organic solvents such as acetonitrile, methanol, methylene chloride.

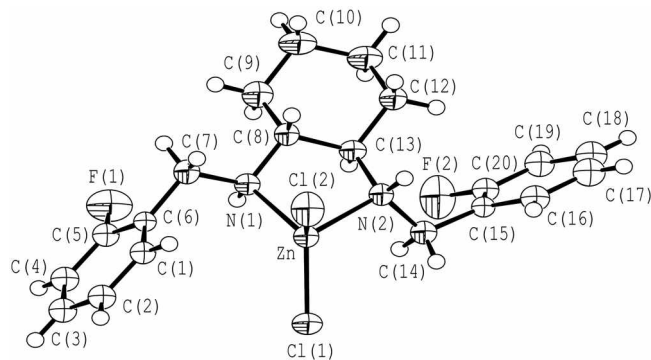
**Crystal structure.** The crystal structure of the chiral Zn(*f-L*)Cl<sub>2</sub> is confirmed by X-ray analysis as shown in Figure 1. The central Zn ion was coordinated by two nitrogen atoms of *f-L* and two chloro atoms in a distorted tetrahedral arrangement. The bond distances Zn-N(1) and Zn-N(2) are



**Scheme 1.** (i)  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Na}_2\text{CO}_3$ , 2-F- $\text{C}_6\text{H}_4\text{CHO}$ , rt, a day; (ii)  $\text{NaBH}_4$ , MeOH; (iii)  $\text{ZnCl}_2$ , EtOH, rt, overnight.



**Scheme 2.** Catalytic nitroaldol reaction.



**Figure 1.** An ORTEP drawing of  $\text{Zn}(f\text{-L})\text{Cl}_2$  with the numbering scheme. Thermal ellipsoids are drawn at 40% probability.

2.056(4) and 2.095(4) Å respectively, which are close to those in a similar complex of  $\text{Zn}(R,R\text{-bmbcd})\text{Cl}_2$  [bmbcd:  $N,N'$ -bis(4-methoxy-benzyl)-( $R,R$ )-1,2-cyclohexane diamine], i.e., 2.066(2) and 2.092(2) Å.<sup>13</sup> The bond distances Zn-Cl(1) and Zn-Cl(2) are 2.182(2) and 2.234(2) Å, also close to those in the similar complex, 2.2289(2) and 2.2036(8) Å respectively.<sup>13</sup> The bond angles of N-Zn-Cl are in the range of 104.9(1)-120.9(1)° which are more variable than the bond angles of N-Zn-Cl in  $\text{Zn}(R,R\text{-bmbcd})\text{Cl}_2$ , 108.43(7)-113.32(7)°. The bond angles of N(1)-Zn-N(2) and Cl(1)-Zn-Cl(2) are 86.2(1) and 119.52(7)°, similar to those in  $\text{Zn}(R,R\text{-bmbcd})\text{Cl}_2$ , 85.66(9) and 121.42(3)° respectively. The coordination of ( $R,R$ )-1,2-diaminocyclohexane moiety to Zn leads to a 5-membered zincaheterocyclic ring that blocks nitrogen and increases the N-inversion barrier, and thus induces chirality because there is non-equivalence of the nitrogen substituents. The X-ray structure revealed that two  $S$  configurations for both N(1) and N(2) atoms respectively ( $S,S$ ), which was found in  $\text{Zn}(R,R\text{-bmbcd})\text{Cl}_2$  and Ni-complex<sup>12(b)</sup> but two nitrogen atoms in similar Pd-complex possessed  $R$  and  $S$  configurations.<sup>12(a)</sup>  $^1\text{H-NMR}$  data of the complex shows that the original  $C_2$ -symmetry of the diamino ligand

still exists from only one single pick at  $\delta$  2.64 for 2H of both -NH groups, which means almost similar environment around N atoms.

**Catalytic nitroaldol reaction.** 10 mol% of  $\text{Zn}(L)\text{Cl}_2$  as the chiral Lewis acid catalyst and 3 mol% of bases as promoters were used for nitroaldol reaction at low temperature,  $-10^\circ\text{C}$  (Scheme 2), herein methanol used as the solvent.

The reaction took place in a slow rate, after a week the conversion was in the range of 70-78%. With ( $i\text{-Pr}$ )<sub>2</sub>NEt, the reaction rate is a little faster than in the case of Et<sub>3</sub>N, however, the ee is similar, 31 to 34% respectively. In the both cases the ee was not so high. The diamine ligand is still simple and the complex structure is quite flexible around the center metal so the steric hinderance is not strong enough to afford high ee, which may be the reasons for the low ee.

## Conclusion

We have synthesized a new chiral Lewis acid,  $\text{Zn}(f\text{-L})\text{Cl}_2$ , successfully as an enantioselective catalyst for asymmetric nitroaldol reaction. A ligand,  $f\text{-L}$ , and a new chiral Zn(II) complex were formed in the high yield by a convenient procedure. Zn(II) was coordinated with 2 nitrogen atoms and 2 chloro ligands in a distorted tetrahedral geometry. Although the ee is still not so high, the attempts to obtain new novel ligands and new complexes should be continuous. This study may contribute to the development of inexpensive chiral catalysts for nitroaldol reaction and asymmetric synthesis as well.

**Supplementary data.** CCDC 655786 contains the supplementary crystallographic data for  $\text{Zn}(f\text{-L})\text{Cl}_2$ . These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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