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**ZINC(II) COMPLEXES WITH THE TETRADENTATE SCHIFF BASE LIGAND  
*N,N'*-BIS(1-PYRIDIN-2-YL-ETHYLIDENE)PROPANE-1,3-DIAMINE:  
SYNTHESIS AND CRYSTAL STRUCTURES**

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Two new zinc(II) complexes  $[\text{ZnL}(\text{N}_3)] \cdot \text{BF}_4$  (1) and  $[\text{ZnBrL}] \cdot \text{BF}_4$  (2), derived from the tetradentate Schiff base ligand *N,N'*-bis(1-pyridin-2-yl-ethylidene)propane-1,3-diamine (L), are prepared and characterized by physicochemical methods and single crystal X-ray crystallography. The crystal of (1) is triclinic: space group *P*-1,  $a = 8.593(1) \text{ \AA}$ ,  $b = 8.752(1) \text{ \AA}$ ,  $c = 13.393(2) \text{ \AA}$ ,  $\alpha = 97.153(1)^\circ$ ,  $\beta = 93.046(1)^\circ$ ,  $\gamma = 91.577(1)^\circ$ ,  $V = 997.4(2) \text{ \AA}^3$ ,  $Z = 2$ . The crystal of (2) is triclinic: space group *P*-1,  $a = 8.351(1) \text{ \AA}$ ,  $b = 8.956(1) \text{ \AA}$ ,  $c = 13.139(2) \text{ \AA}$ ,  $\alpha = 92.716(1)^\circ$ ,  $\beta = 94.241(2)^\circ$ ,  $\gamma = 95.016(1)^\circ$ ,  $V = 974.8(2) \text{ \AA}^3$ ,  $Z = 2$ . The geometries of the penta-coordinated zinc atoms in both complexes are intermediate between the square pyramid and the trigonal bipyramid having the Addison parameters of 0.39 and 0.47 respectively. The syntheses of the complexes show distinct preference for the anions in the order  $\text{Br}^- > \text{N}_3^- > \text{CH}_3\text{COO}^-$ .

**Keywords:** zinc(II), Schiff base, synthesis, crystal structure.

Schiff bases have been attracted considerable interest in the preparation and application of the complexes with various metal ions [ 1—3 ]. The Schiff bases derived from salicylaldehyde and its derivatives represent an important class of ligands in coordination chemistry, and a large number of metal complexes with them have been reported [ 4—6 ]. Pyridine-2-carbaldehyde is also an interesting precursor for the synthesis of Schiff bases. The lanthanide and transition metal complexes derived from the Schiff base *N,N'*-bis(1-pyridin-2-yl-methylidene)propane-1,3-diamine have widely been reported [ 7—10 ]. However, for the similar Schiff base *N,N'*-bis(1-pyridin-2-yl-ethylidene)propane-1,3-diamine (L) only one cadmium(II) [ 11 ] and a few copper(II) complexes [ 12—14 ] have been reported. In the present paper, two new zinc(II) complexes  $[\text{ZnL}(\text{N}_3)] \cdot \text{BF}_4$  (1) and  $[\text{ZnBrL}] \cdot \text{BF}_4$  (2) have been prepared and characterized.

#### EXPERIMENTAL

**Materials and methods.** The analytical purity of 2-acetylpyridine and propane-1,3-diamine were purchased from Lancaster. Sodium azide, ammonium fluoroborate, zinc acetate dihydrate, and zinc bromide were obtained from Beijing Chemical Reagent Company and were used as received. Elemental analyses (carbon, hydrogen, and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O Elemental Analyzer. Zinc analysis was carried out by EDTA titration. IR spectra (KBr discs, 4000—400  $\text{cm}^{-1}$ ) were recorded using a JASCO FT-IR model 420 spectrometer. Molar conductance was measured using a Systronics conductivity meter where the cell constant was calibrated with the 0.01 M KCl solution, and anhydrous methanol was used as the solvent.

**Caution!** Although no problems were encountered in this work, sodium azide and the complexes containing sodium ligands are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

**Synthesis of L.** The Schiff base ligand L was prepared by a reaction of propane-1,3-diamine (0.1 mol, 7.4 g) and 2-acetylpyridine (0.2 mol, 24.2 g) in methanol (500 ml) at ambient temperature. The Schiff base ligand was not isolated and the clear yellow solution was used directly for the synthesis of the complexes.

**Synthesis of (1).** A yellow solution of L (5 ml, 1 mmol) was diluted by 30 ml of methanol, to which was added with stirring an aqueous solution (5 ml) of sodium azide (65 mg, 1 mmol) and ammonium fluoroborate (105 mg, 1 mmol), and a methanol solution of zinc acetate dihydrate (220 mg, 1 mmol). The mixture was stirred at ambient temperature for 30 min to give a clear colorless solution. Colorless block-shaped single crystals suitable for X-ray diffraction were formed after slow evaporation of the solvent for a few days. The solvent was further evaporated for three quarters of the original volume, and the crystals were isolated by filtration. The yield was 341 mg (72 %). Analysis: Calcd. for  $C_{17}H_{20}BF_4N_7Zn$ : C 43.0, H 4.2, N 20.7, Zn 13.8 %. Found: C 42.7, H 4.3, N 20.8, Zn 14.1 %.

**Synthesis of (2).** Complex (2) was prepared according to the method described for (1), only with zinc acetate dihydrate replaced by zinc bromide (225 mg, 1 mmol). The yield was 405 mg (79 %). Analysis: Calcd. for  $C_{17}H_{20}BBrF_4N_4Zn$ : C 39.8, H 3.9, N 10.9, Zn 12.8 %. Found: C 39.6, H 4.0, N 10.7, Zn 13.2 %.

**X-ray crystallography.** Data collection for both complexes was performed by the  $\omega$ -scan method within the limits  $2.35 \leq \theta \leq 27.00^\circ$  and  $2.29 \leq \theta \leq 27.00^\circ$  for (1) and (2) respectively on a Bruker AXS CCD diffractometer with graphite-monochromated  $MoK_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection and cell refinement were carried out with SMART [15], data reduction with SAINT [15], and experimental absorption correction with SADABS [16]. The structures were solved by direct methods (SHELXS-97) [17]; the refinement was made by full-matrix least squares on  $F^2$  using the SHELXL-97 program suit [17]. All non-hydrogen positions were found and refined with anisotropic temperature factors. The hydrogen atoms were calculated with appropriate riding models. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data for the complexes (1) and (2) have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 781803 for (1) and 781804 for (2). This information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; website: <http://www.ccdc.cam.ac.uk>).

## RESULTS AND DISCUSSION

The Schiff base ligand L was prepared by the condensation of one equivalent of propane-1,3-diamine and two equivalents of 2-acetylpyridine in methanol. Considering the neutral nature of the ligand, additional counteranions are needed when coordinating to the metal ions. Except for the common anions, such as halides or pseudohalides [7, 8, 18], perchlorate is widely used in the preparation of these complexes [12, 13, 19]. Fluoroborate is an anion similar to perchlorate and a number of complexes with it have been reported [20–22], however, no complexes with L bearing such anions have been reported so far. In the present work, a reaction of L,  $NaN_3$ ,  $NH_4BF_4$ , and  $Zn(CH_3COO)_2$  for (1) or  $ZnBr_2$  for (2) yielded two mononuclear zinc complexes with fluoroborate anions. The syntheses of the complexes show distinct preference for the anions in the order  $Br^- > N_3^- > CH_3COO^-$ . The order is in agreement with the ligand field strength of the anions towards zinc [23].

The air-stable and moisture-insensitive complexes are soluble in common organic solvents such as methanol, ethanol, dichloromethane, acetonitrile, and DMF, but are insoluble in water. In methanol solutions, both complexes behave as 1:1 electrolytes [24] as reflected in their  $\Lambda_M$  values:  $127 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  and  $133 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  for (1) and (2) respectively.

The intense bands at  $1623 \text{ cm}^{-1}$  for both complexes are assigned to the stretching vibrations of the azomethine groups. For (1), the bands indicative of the terminal azide group are at  $2067 \text{ cm}^{-1}$ . The

Table 1

*Crystallographic data and refinement parameters for complexes (1) and (2)*

Complex	(1)	(2)
Formula	C <sub>17</sub> H <sub>20</sub> BF <sub>4</sub> N <sub>7</sub> Zn	C <sub>17</sub> H <sub>20</sub> BBrF <sub>4</sub> N <sub>4</sub> Zn
<i>M</i>	474.6	512.5
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å	8.593(1), 8.752(1), 13.393(2)	8.351(1), 8.956(1), 13.139(2)
α, β, γ, deg.	97.153(1), 93.046(1), 91.577(1)	92.716(1), 94.241(2), 95.016(1)
<i>V</i> , Å <sup>3</sup>	997.4(2)	974.8(2)
<i>Z</i>	2	2
ρ <sub>calcd</sub> , g·cm <sup>-3</sup>	1.580	1.746
<i>T</i> , K	298(2)	298(2)
μ, mm <sup>-1</sup>	1.287	3.356
Collected / Independent reflections	8200 / 4244	6964 / 4119
<i>R</i> <sub>int</sub>	0.0195	0.0223
Observed reflections ( <i>I</i> > 2σ( <i>I</i> ))	3549	3121
Parameters	273	254
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0386, 0.1047	0.0338, 0.0745
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0483, 0.1112	0.0538, 0.0840
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035	1.019
Δρ <sub>max</sub> and Δρ <sub>min</sub> , e/Å <sup>-3</sup>	0.773 and -0.443	0.371 and -0.639

Table 2

*Coordinate bond lengths (Å) and angles (deg.) for complexes (1) and (2)*

(1)					
Zn1—N1	2.143(2)	N5—Zn1—N2	117.6(1)	N5—Zn1—N3	108.6(1)
Zn1—N3	2.102(2)	N2—Zn1—N3	87.8(1)	N5—Zn1—N4	112.4(1)
Zn1—N2	2.093(2)	N2—Zn1—N4	130.0(1)	N3—Zn1—N4	76.6(1)
Zn1—N4	2.125(2)	N5—Zn1—N1	97.7(1)	N2—Zn1—N1	76.2(1)
		N3—Zn1—N1	153.3(1)	N4—Zn1—N1	97.3(1)
(2)					
Zn1—N1	2.116(2)	N3—Zn1—N2	87.3(1)	N3—Zn1—N1	126.7(1)
Zn1—N3	2.098(3)	N2—Zn1—N1	76.9(1)	N3—Zn1—N4	76.4(1)
Zn1—N5	1.966(2)	N2—Zn1—N4	154.9(1)	N1—Zn1—N4	97.5(1)
Zn1—N2	2.112(3)	N3—Zn1—Br1	123.2(1)	N2—Zn1—Br1	104.2(1)
Zn1—N4	2.130(2)	N1—Zn1—Br1	110.0(1)	N4—Zn1—Br1	100.7(1)
Zn1—Br1	2.393(1)				

Zn—N absorption bands are in the 530—450 cm<sup>-1</sup> region. The strong band at 621 cm<sup>-1</sup> and the weak band at 413 cm<sup>-1</sup> could be assigned to the in-plane and out-of-plane pyridine ring bending vibrations. The occurrence of bands at about 1066 cm<sup>-1</sup> (broad, strong) and bands at about 522 cm<sup>-1</sup> (sharp, medium) in the IR spectra of both complexes indicates that the fluoroborate anions are present in their regular tetrahedral geometry, which is in accordance with that observed in most examples where the fluoroborate anions are not coordinated to the metal atoms [20—22].

The molecular structures of complexes (1) and (2) are shown in Figs. 1 and 2 respectively. Each complex consists of a mononuclear zinc complex cation and a fluoroborate anion. The coordination

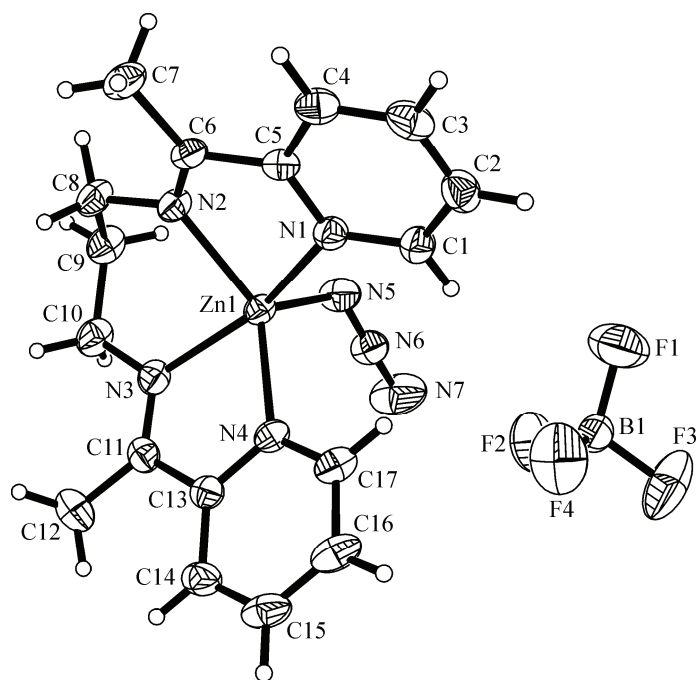


Fig. 1. Perspective view and atom numbering scheme of (1). All the non-hydrogen atoms are represented by 30 % thermal probability ellipsoids

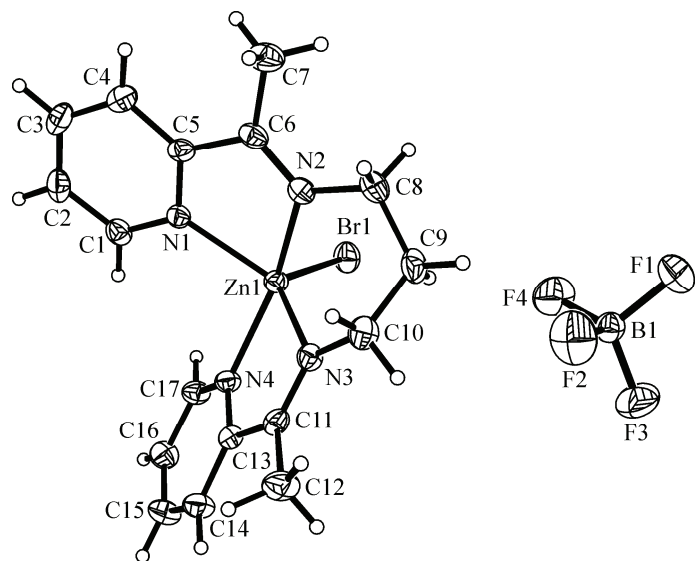


Fig. 2. Perspective view and atom numbering scheme of (2). All the non-hydrogen atoms are represented by 30 % thermal probability ellipsoids

geometries around the zinc atoms in both complexes are best described as elongated square pyramids, furnished by two imine N and two pyridine N atoms of a Schiff base ligand at the basal plane, and by an N atom of an azide ligand in (1) or a bromide atom in (2) at the apical position. Deviations of the coordinating N1, N2, N3, and N4 atoms from the least-squares mean planes through them are  $-0.194 \text{ \AA}$ ,  $0.214 \text{ \AA}$ ,  $-0.212 \text{ \AA}$ , and  $0.192 \text{ \AA}$  respectively in (1), and  $-0.231 \text{ \AA}$ ,  $0.256 \text{ \AA}$ ,  $-0.260 \text{ \AA}$ , and  $0.235 \text{ \AA}$  respectively in (2). This deviation from the planarity of the equatorial plane can also be indicated by N1—Zn1—N3 and N2—Zn1—N4 *trans* angles that are  $153.3(1)^\circ$  and  $130.0(1)^\circ$  in (1) and  $126.7(1)^\circ$  and  $154.9(1)^\circ$  in (2) respectively. The Zn atoms are displaced by  $0.68\text{--}0.69 \text{ \AA}$  from the corresponding plane toward the apical donor atoms.

The Addison parameter values ( $\tau$ ) [25] are 0.39 and 0.47 in complexes (1) and (2) respectively, indicating that the coordination geometries are between a square pyramid and a trigonal bipyramid. The chelate rings formed by the Zn1, N2, C8—C10, and N3 atoms in complexes (1) and (2) have *boat* conformations. In (1), the diagonally positioned atoms, Zn1 and C9, are shifted from the least-squares plane defined by the N2, N8, C10, and N3 atoms by 0.738(1) Å and 0.709(2) Å respectively, and those in (2), are shifted by 0.709(1) Å and 0.698(2) Å respectively. The azide group in (1) is nearly linear with the N5—N6—N7 angle of 176.5(3)°.

The dihedral angles between the two pyridine ring planes are 65.0(3)° for (1) and 61.7(3)° for (2). All the coordinate bond lengths and angles in both complexes are comparable to those observed in the zinc(II) complexes with Schiff bases [26—28].

The tetrafluoroborate anions in both complexes involve approximately tetrahedral stereochemistry with acceptable mean B—F distances of 1.346(4) Å for (1) and 1.365(4) Å for (2), and mean F—B—F angles of 109.4(3)° for both complexes, which were as expected and normally found in the tetrahedral BF<sub>4</sub> anions.

### CONCLUSIONS

In this paper, two new zinc(II) complexes with the Schiff base ligand *N,N'*-bis(1-pyridin-2-yl-ethylidene)propane-1,3-diamine were prepared and characterized by elemental analysis, IR spectra and single crystal X-ray analysis. The Schiff base coordinates to the Zn atoms through the four N atoms. The tetrafluoroborate anions are resided in the complexes to balance the charge. The syntheses of the complexes show distinct preference for the anions in the order Br<sup>-</sup> > N<sub>3</sub><sup>-</sup> > CH<sub>3</sub>COO<sup>-</sup>.

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