

## КРАТКИЕ СООБЩЕНИЯ

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## CRYSTAL STRUCTURE OF AN END-ON AZIDO-BRIDGED POLYMERIC ZINC(II) COMPLEX

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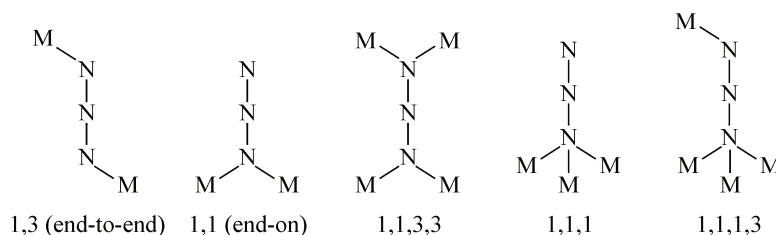
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A new end-on azido-bridged polymeric zinc(II) complex  $[\text{Zn}_2\text{CIL}(\mu_{1,1}\text{-N}_3)]_n$ , where L is the dianionic form of *N,N'*-bis(5-fluoro-2-hydroxybenzylidene)-2-hydroxy-1,3-propanediamine, is prepared and structurally characterized by elemental analysis and single crystal X-ray diffraction. The complex crystallizes in the monoclinic space group  $P2_1/c$ , with unit cell dimensions  $a = 9.194(1) \text{ \AA}$ ,  $b = 22.356(2) \text{ \AA}$ ,  $c = 9.598(1) \text{ \AA}$ ,  $\beta = 95.869(3)^\circ$ ,  $V = 1962.5(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $R_1 = 0.0691$ , and  $wR_2 = 0.1642$ . The inner Zn atom of the  $[\text{Zn}_2\text{CIL}]$  unit is coordinated by the imino N and phenolate O atoms of L and one azido N atom, forming a square pyramidal geometry. The outer Zn atom of the  $[\text{Zn}_2\text{CIL}]$  unit is coordinated by two phenolate O of L, one Cl ligand, and one N atom of the bridging azide group, forming a tetrahedral geometry. The Zn...Zn distance in the  $[\text{Zn}_2\text{CIL}]$  unit is  $3.072(2) \text{ \AA}$ . The  $[\text{Zn}_2\text{CIL}]$  units are linked through end-on azido bridges, forming 1D chains running along the *c* axis.

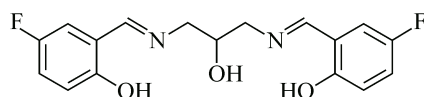
**Key words:** Schiff base, zinc, polymeric complex, crystal structure, azide.

Polymeric structures of complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications [1–3]. Bis-Schiff bases derived from salicylaldehyde and its derivatives with diamines are a kind of versatile ligands in coordination chemistry. The preferred way to construct polynuclear complexes is the use of suitable bridging groups, such as  $\text{N}_3^-$ ,  $\text{NCS}^-$ ,  $\text{N}(\text{CH}_2)_2^-$ , dicarboxylate, 4,4'-bipy, and so on [4–7]. Among the bridging groups, the azide ligand has received particular interest because it is very useful to design extended polynuclear complexes. It can bind up to three metal atoms when acting as a monatomic bridge (end-on, EO) and up to six using the two terminal nitrogen atoms to bridge (end-to-end, EE) (Scheme 1) [8–10]. A major obstacle to a more comprehensive study of such azide-based polymeric coordination complexes is the lack of rational synthetic procedures, since with the present state of knowledge it is hardly possible to determine which coordination mode will be adopted by the azide ligand and whether the sought-after alternating chain structure will finally be formed or not. Hydrogen bonds are known as an important factor for the self-assembly of complexes [11–13]. *N,N'*-Bis(2-hydroxybenzylidene)-2-hydroxy-1,3-propanediamine and its derivatives have been used as bis-Schiff bases in the construction of complexes with various metal atoms [14–17]. However, no zinc complexes derived from such bis-Schiff bases have been reported. As a continuation of the work on the self-assembly preparation of azido-bridged polymeric complexes, in this paper, a new end-on azido-bridged polymeric zinc(II) complex  $[\text{Zn}_2\text{CIL}(\mu_{1,1}\text{-N}_3)]_n$ , where L is the dianionic form of *N,N'*-bis(5-fluoro-2-hydroxybenzylidene)-2-hydroxy-1,3-propanediamine ( $\text{H}_2\text{L}$ , Scheme 2), was prepared and structurally characterized.

**Experimental. Materials and methods.** Starting materials, reagents, and solvents with analytical grade were purchased from commercial suppliers and used without further purification. Elemental



Scheme 1. Bridging modes of the azide ligand

Scheme 2. Schiff base H<sub>2</sub>L ligand

analyses were performed on a Perkin-Elmer 240C elemental analyzer. Single crystal structural X-ray diffraction was carried out on a Bruker D8 VENTURE PHOTON diffractometer. Molar conductance of the complexes at a concentration of  $10^{-3}$  M in absolute methanol was measured with a Shanghai DDS-11A conductometer.

**Synthesis of the complex.** 5-Fluorosalicylaldehyde (2.0 mmol, 0.28 g) and 1,3-diaminopropan-2-ol (1.0 mmol, 0.09 g) were mixed and magnetically stirred in methanol (30 ml) for 30 min. Then, a methanol solution (20 ml) containing sodium azide (1.0 mmol, 0.065 g) and zinc chloride (1.0 mmol, 0.14 g) were added dropwise to the solution. Then final mixture was further stirred at room temperature for 1 h to give a colorless solution. After keeping the solution in air for a few days, colorless block-shaped crystals of the complex, suitable for the X-ray crystal structural determination, were formed on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol, and dried in air. Yield 32 %. Anal. calcd. For C<sub>17</sub>H<sub>14</sub>ClF<sub>2</sub>N<sub>5</sub>O<sub>3</sub>Zn<sub>2</sub>: C, 37.8; H, 2.6; N, 13.0; Found: C, 37.5; H, 2.7; N, 12.8 %.

**Data collection, structural determination, and refinement.** Diffraction intensities for the complex were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK<sub>α</sub> radiation ( $\lambda = 0.71073$  Å). The collected data were reduced using the SAINT program [18], and multi-scan absorption corrections were performed using the SADABS program [19]. The structure was solved by a direct method and refined against  $F^2$  by the full-matrix least-squares method using SHELXTL [20]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

**Results and discussion.** The Schiff base H<sub>2</sub>L was prepared by the condensation reaction in the 2:1 molar ratio of 5-fluorosalicylaldehyde with 1,3-diaminopropan-2-ol in methanol. The ligand was not isolated and purified, which was used to prepare the complex directly. The complex was prepared by the reaction of the Schiff base ligand, zinc chloride, and sodium azide in methanol under room temperature. The complex is stable in air, soluble in common polar organic solvents such as DMSO, DMF, methanol, ethanol, and acetonitrile, but insoluble in water. The molar conductance value for the complex measured in methanol at a concentration of  $10^{-3}$  M is  $33 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , suggesting it is non-electrolyte [21].

**Structural description of the complex.** The molecular structure of the complex is shown in Fig. 1. X-ray crystallography reveals that the complex is an end-on azido-bridged polymeric zinc(II) species. The smallest repeating moiety is [Zn<sub>2</sub>CIL(N<sub>3</sub>)]. The Z···Zn distance in the [Zn<sub>2</sub>CIL] unit is 3.072(2) Å.

The inner Zn atom of the [Zn<sub>2</sub>CIL] unit is in a square pyramidal coordination, with two phenolate O and two imino N atoms defining the basal plane, and with one azido N atom occupying the apical position. The Zn atom lies by 0.398(3) Å from the least-squares plane defined by the four basal donor atoms in the direction of the apical ligand. The distortion of the square pyramidal geometry can be observed by the coordinate bond angles, ranging from 96.9(3)° to 105.9(3)° for the apical and basal do-

Table 1

*Crystallographic data for the complex*

Parameter	Value
CCDC	956335
Empirical formula	C <sub>17</sub> H <sub>14</sub> ClF <sub>2</sub> N <sub>5</sub> O <sub>3</sub> Zn <sub>2</sub>
Formula weight	540.5
Temperature, K	298(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	9.194(1), 22.356(2), 9.598(1)
β, deg.	95.869(3)
<i>V</i> , Å <sup>3</sup>	1962.5(4)
<i>Z</i>	4
μ, mm <sup>-1</sup>	2.629
<i>D</i> <sub>c</sub> , g/cm <sup>3</sup>	1.829
Reflections collected	17462
Unique reflections	3440
Observed reflections [ <i>I</i> ≥ 2σ( <i>I</i> )]	2552
Parameters	272
Restraints	0
<i>F</i> (000)	1080
<i>R</i> <sub>int</sub>	0.0696
Goodness of fit on <i>F</i> <sup>2</sup>	1.072
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0691 / 0.1642
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.1010 / 0.1808
Largest diff. Peak and hole, e/Å <sup>3</sup>	1.699, -0.635

Table 2

*Selected bond lengths (Å) and angles (deg.) for the complex*

Zn1—N1	2.045(7)	N2—Zn1—N1	98.8(3)	N2—Zn1—O2	89.2(2)
Zn1—O1	2.071(5)	N1—Zn1—O2	156.1(3)	N2—Zn1—O1	153.5(3)
Zn1—N5	2.073(7)	N1—Zn1—O1	86.9(2)	O2—Zn1—O1	76.5(2)
Zn2—O2	1.977(5)	N2—Zn1—N5	105.9(3)	N1—Zn1—N5	102.5(3)
Zn2—Cl1	2.208(2)	O2—Zn1—N5	96.9(3)	O1—Zn1—N5	97.9(3)
Zn1—N2	2.036(7)	O1—Zn2—O2	80.9(2)	O1—Zn2—N5A	118.1(3)
Zn1—O2	2.065(6)	O2—Zn2—N5A	109.0(3)	O1—Zn2—Cl1	112.48(18)
Zn2—O1	1.971(5)	O2—Zn2—Cl1	124.2(2)	N5A—Zn2—Cl1	110.0(2)
Zn2—N5A	1.997(7)				

Symmetry code for A: *x*, 1/2-*y*, 1/2+*z*.

nors, and from 76.5(2)° to 98.8(3)° for the basal donors. The main factor leading for the distortion may be the tensile force of the four-membered chelate ring Zn1—O1—Zn2—O2. The bond lengths related to the Zn1 atom are within normal ranges when compared to other similar structures bearing five-coordinated zinc centers [22, 23]. The question arises as to whether the coordination polyhedron around the Zn atom can be described as a distorted square pyramid or a trigonal bipyramid. Further information can be obtained by determining the structural index τ [24], which represents the relative

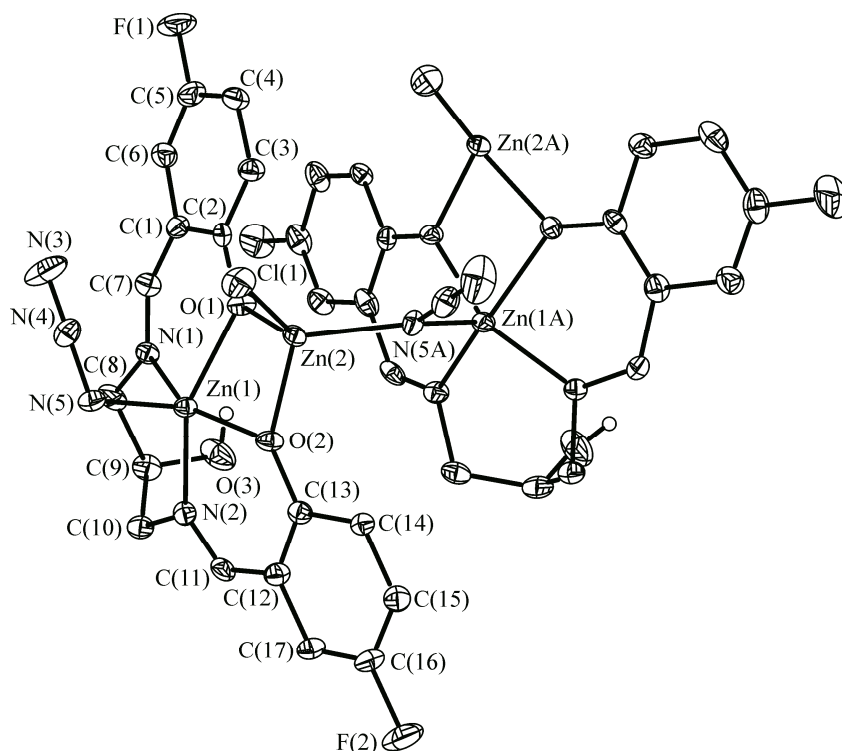


Fig. 1. A perspective view of the asymmetric unit of the complex. Thermal ellipsoids are drawn at the 30 % probability level. Symmetry code for related atoms:  $x, 1/2-y, 1/2+z$

amount of trigonality (square pyramid,  $\tau = 0$ ; trigonal bipyramid,  $\tau = 1$ );  $\tau = (\beta - \alpha)/60^\circ$ ,  $\alpha$  and  $\beta$  being the two largest angles around the central atom. The value of  $\tau$  is 0.043. Thus, the coordination geometry of Zn1 is best described as a square pyramid.

The outer atom of the  $[\text{Zn}_2\text{CIL}]$  unit is coordinated by two phenolate O atoms of the Schiff base ligand, one Cl ligand, and one azido N atom, forming a tetrahedral coordination. The distortion of the tetrahedral geometry can be observed both by the coordinate bond lengths and angles. The Zn2—C11 bond is much longer than the others. The bond angles are ranging from  $80.9(2)^\circ$  to  $124.2(2)^\circ$ , which might be caused by the tensile force of the four-membered chelate ring Zn1—O1—Zn2—O2. The bond lengths related to the Zn2 atom are within normal ranges when compared to other similar structures bearing four-coordinated zinc centers [ 25, 26 ].

In the crystal structure of the complex, the  $[\text{Zn}_2\text{CIL}]$  units are linked through end-on azido bridges, forming 1D chains running along the  $c$  axis (Fig. 2).

**IR spectra.** The IR spectra of the Schiff base and the complex provide information about the metal-ligand bonding. The weak and broad absorptions in the range  $3270\text{--}3380\text{ cm}^{-1}$  are assigned to the vibration of O—H groups of the free Schiff base and the complex. The strong absorption band at  $1623\text{ cm}^{-1}$  for  $\text{H}_2\text{L}$  is assigned to the azomethine groups,  $\nu(\text{C}=\text{N})$  [ 27 ]. The band is shifted to a lower wavenumber ( $1607\text{ cm}^{-1}$ ) in the spectrum of the complex, which can be attributed to the coordination of the azomethine nitrogen atoms to the zinc atoms. The medium absorption band of the Ar—O bond for the free Schiff base is located at  $1245\text{ cm}^{-1}$ , which is observed at a lower wavenumber for the complex ( $1223\text{ cm}^{-1}$ ). The intense band indicative of the azide ligands is located at  $2040\text{ cm}^{-1}$  for the complex [ 28 ]. New weak absorption bands indicative of the Zn—O and Zn—N bonds are observed in the range  $400\text{--}600\text{ cm}^{-1}$ .

**Supplementary information.** CCDC-956335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrie->

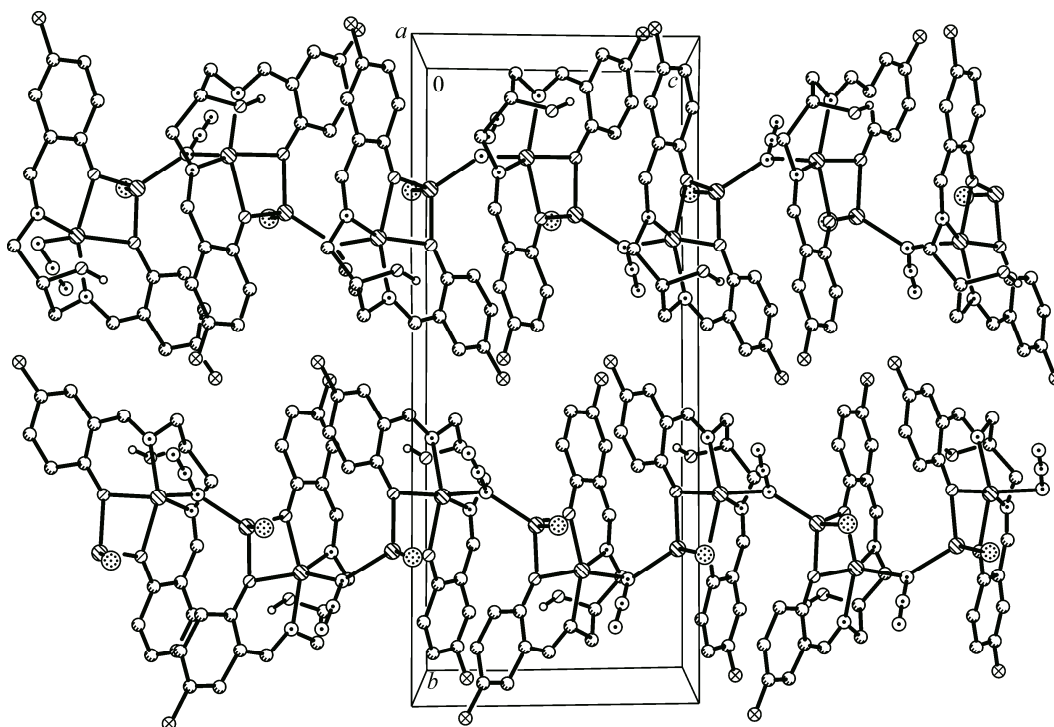


Fig. 2. Molecular packing of the complex, viewed along the *a* axis

ving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

#### REFERENCES

1. Massoud S.S., Vicente R., Fontenot P.R. *et al.* // *Polyhedron*. – 2012. – **46**, N 1. – P. 66 – 73.
2. Ni L.-L., You Z.-L., Zhang L. *et al.* // *Transition Met. Chem.* – 2010. – **35**, N 1. – P. 13 – 17.
3. You Z.-L., Lu Y., Zhang N. *et al.* // *Polyhedron*. – 2011. – **30**, N 13. – P. 2186 – 2194.
4. Mautner F.A., Albering J.H., Mikuriya M. *et al.* // *Inorg. Chem.* – 2010. – **13**, N 6. – P. 796 – 799.
5. Andreev G., Budantseva N., Fedoseev A. *et al.* // *Inorg. Chem.* – 2011. – **50**, N 22. – P. 11481 – 11486.
6. Banu K.S., Mondal S., Guha A. *et al.* // *Polyhedron*. – 2011. – **30**, N 1. – P. 163 – 168.
7. Das A., Demeshko S., Dechert S. *et al.* // *Eur. J. Inorg. Chem.* – 2011. – N 8. – P. 1240 – 1248.
8. Liu F.-C., Zhao J.-P., Hu B.-W. *et al.* // *Dalton Trans.* – 2010. – **39**, N 5. – P. 1185 – 1187.
9. Wang Q.-L., Jia X.-Q., Liao D.-Z. *et al.* // *Transition Met. Chem.* – 2006. – **31**, N 4. – P. 434 – 440.
10. Aronica C., Jeanneau E., El Moll H. *et al.* // *Chem. Eur. J.* – 2007. – **13**, N 13. – P. 3666 – 3674.
11. Talarico A.M., Szerb E.I., Mastropietro T.F. *et al.* // *Dalton Trans.* – 2012. – **41**, N 16. – P. 4919 – 4926.
12. Taylor R.A., Law D.J., Sunley G.J. *et al.* // *Chem. Commun.* – 2008. – N 24. – P. 2800 – 2802.
13. Constable E.C., Zhang G.Q., Housecroft C.E. *et al.* // *Chem. Commun.* – 2010. – **46**, N 18. – P. 3077 – 3079.
14. Lee C.-J., Cheng S.-C., Lin H.-H. *et al.* // *Inorg. Chem. Commun.* – 2005. – **8**, N 3. – P. 235 – 238.
15. Mukherjee A., Saha M.K., Nethaji M. *et al.* // *Polyhedron*. – 2004. – **23**, N 13. – P. 2177 – 2182.
16. Naik S.G., Mukherjee A., Raghunathan R. *et al.* // *Polyhedron*. – 2006. – **25**, N 10. – P. 2135 – 2141.
17. Basak S., Sen S., Rosair G. *et al.* // *Aust. J. Chem.* – 2009. – **62**, N 4. – P. 366 – 375.
18. Bruker, SMART and SAINT, Madison (WI, USA): Bruker AXS Inc., 2002.
19. Sheldrick G.M. SADABS, Program for Empirical Absorption Correction of Area Detector, Göttingen (Germany): Univ. of Göttingen, 1996.
20. Sheldrick G.M. SHELXTL, Version 5.1, Software Reference Manual, Madison (WI, USA): Bruker AXS Inc., 1997.
21. Geary W.J. // *Coord. Chem. Rev.* – 1971. – **7**, N 1. – P. 81 – 122.
22. Atakol O., Tatar L., Akay M.A. *et al.* // *Anal. Sci.* – 1999. – **15**, N 2. – P. 199 – 200.
23. Adams H., Bailey N.A., Bertrand P. *et al.* // *J. Chem. Soc., Dalton Trans.* – 1995. – N 2. – P. 275 – 279.
24. Addison A.W., Rao T.N., Reedijk J. *et al.* // *Dalton Trans.* – 1984. – N 7. – P. 1349 – 1356.
25. Tatar L., Ulku D., Atakol O. *et al.* // *Anal. Sci.* – 2002. – **18**, N 10. – P. 1171 – 1172.
26. Yang X., Jones R.A., Wu Q. *et al.* // *Polyhedron*. – 2006. – **25**, N 2. – P. 271 – 278.
27. Zhou Y.-M., Ye X.-R., Xin F.-B. *et al.* // *Transition Met. Chem.* – 1999. – **24**, N 1. – P. 118 – 120.
28. Chattopadhyay S., Ray M.S., Drew M.G.B. *et al.* // *Polyhedron*. – 2006. – **25**, N 11. – P. 2241 – 2253.