

## Bis{2-[(2-furylmethyl)iminomethyl]-5-methoxyphenolato- $\kappa^2$ N,O}zinc(II)

**Chunyan Li**

College of Health Science, Wuhan Institute of Physical Education, Wuhan 430079, People's Republic of China

Correspondence e-mail: lichunyan2009@yahoo.com.cn

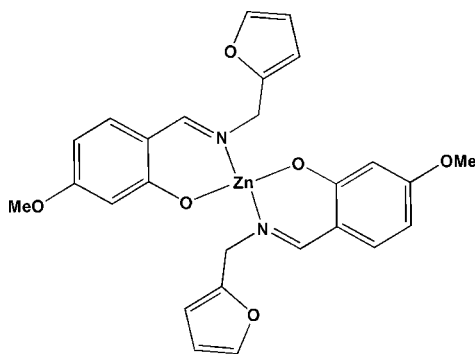
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 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å;  $R$  factor = 0.049;  $wR$  factor = 0.128; data-to-parameter ratio = 14.4.

In the title complex,  $[\text{Zn}(\text{C}_{13}\text{H}_{12}\text{NO}_3)_2]$ , the  $\text{Zn}^{\text{II}}$  ion is located on a twofold rotation axis and is coordinated by two bidentate Schiff base ligands in a distorted tetrahedral environment. The complex molecules are stacked in columns along the  $b$  axis through  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

### Related literature

For the biological activity and applications of  $\text{Zn}(\text{II})$  complexes, see: Csaszar *et al.* (1985); Greener *et al.* (1996); Gultneh *et al.* (1996); Aoki & Kimura (2004). For applications of furfurylamine derivatives, see: Camejo *et al.* (1992); Ledovskikh & Camejo (1993). For a related structure, see; Cai *et al.* (2010).



### Experimental

#### Crystal data

 $[\text{Zn}(\text{C}_{13}\text{H}_{12}\text{NO}_3)_2]$ 
 $M_r = 525.84$ 

 Monoclinic,  $C2/c$   
 $a = 27.210$  (4) Å  
 $b = 5.2244$  (7) Å  
 $c = 19.007$  (3) Å  
 $\beta = 119.507$  (2)°  
 $V = 2351.5$  (5) Å<sup>3</sup>
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.09$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.32 \times 0.20 \times 0.13$  mm

#### Data collection

 Bruker SMART CCD area detector  
 diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2000)  
 $T_{\text{min}} = 0.722$ ,  $T_{\text{max}} = 0.871$ 

 6855 measured reflections  
 2303 independent reflections  
 2062 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.128$   
 $S = 1.01$   
 2303 reflections  
 160 parameters

 1 restraint  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.64$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>
**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                           | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{C9}-\text{H9A}\cdots\text{O1}^i$ | 0.97  | 2.32        | 3.292 (6)   | 177           |

 Symmetry code: (i)  $-x, y - 1, -z + \frac{1}{2}$ 

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2670).

### References

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**supplementary materials**

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## Bis{2-[(2-furylmethyl)iminomethyl]-5-methoxyphenolato- $\kappa^2N,O$ }zinc(II)

C. Li

### Comment

Zinc(II) complexes with the chelate ligands are extensively investigated as models for the active site of carbonic anhydrase and other hydrolytically active enzymes (Greener *et al.*, 1996; Gultneh *et al.*, 1996). Zinc(II) complexes are also studied on the role of zinc(II) structural properties in protein folding (Aoki & Kimura, 2004). Interestingly, zinc(II) complexes are becoming important in pharmaceutical, dye, plastic industries and for liquid crystal technology (Csaszar *et al.*, 1985). In addition, the furfuryl amine and its derivatives are widely used as bioactive antibacterial agents and as steel corrosion inhibitors in recent research (Ledovskikh & Camejo, 1993; Camejo *et al.*, 1992). By taking the biological importance of furfurylamine into account, we designed the title complex containing nitrogen-oxygen donor atoms coordinated with zinc(II).

The title complex reported here is the mononuclear zinc(II) complex of Schiff-base ligand, derived from the condensation of 4-methoxysalicylaldehyde and furfuryl amine (Fig. 1). The zinc(II) atom has a distorted tetrahedral coordination formed by two N atoms and two O atoms from two Schiff-base ligands. The bond distances of Zn—O and Zn—N are 1.925 (3) and 1.984 (3) Å, respectively. The dihedral angle between the coordination planes (N1/Zn1/O1 and N1A/Zn1A/O1A) is 87.24 (8)° (symmetry code A:  $-x, y, 1/2 - z$ ), which is slightly larger than that of 84.43 (6)° between the corresponding coordination planes around zinc(II) atom observed in the similar Schiff base zinc(II) complex, bis(3,5-dibromo-N-benzylsalicylaldimino-N,O)zinc(II) (Cai *et al.*, 2010). The O1—Zn1—O1 angle is 109.27 (18)° and the N1—Zn1—N1 angle is 120.08 (18)°. The other angles subtended at the Zn(II) ion in (ZnN<sub>2</sub>O<sub>2</sub>) is in the range of 96.69 (11)–117.49 (12)°.

In the crystal structure, the molecules are linked *via* intermolecular C—H...O hydrogen bonds forming a column along the *b* axis (Fig. 2).

### Experimental

4-Methoxysalicylaldehyde (304 mg, 2 mmol) and furfurylamine (194 mg, 2 mmol) were dissolved in an aqueous methanol solution (25 mL). The mixture was stirred at room temperature for 1 h to give a clear yellow solution, which was added to a solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (298 mg, 1 mmol) in methanol (10 mL). The mixture was stirred for 30 min at room temperature to give a yellow solution and then filtered. The yellow single crystals suitable for X-ray analysis were obtained by slowly evaporating the above filtrate at room temperature. The crystals were isolated and dried in a vacuum desiccator containing anhydrous CaCl<sub>2</sub>, in about 71% yield. Anal. Calcd for C<sub>26</sub>H<sub>24</sub>ZnN<sub>2</sub>O<sub>6</sub>: C 59.38, H 4.60, N 5.33%. Found: C 59.20, H 4.73 N, 5.30%.

### Refinement

All the H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93–0.97 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . A rigid bond restraint was applied for atoms C11 and C12.

## Figures

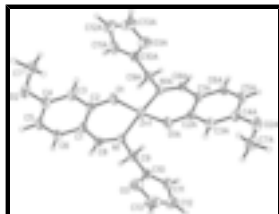


Fig. 1. The molecular structure of the title compound, with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The suffix A corresponds to symmetry code  $-x, y, 1/2 - z$ .



Fig. 2. A packing diagram of the title compound, viewed along the  $b$  axis.

## Bis{2-[(2-furylmethyl)iminomethyl]-5-methoxyphenolato- $\kappa^2N,O$ }zinc(II)

### Crystal data

[Zn(C<sub>13</sub>H<sub>12</sub>NO<sub>3</sub>)<sub>2</sub>]

$M_r = 525.84$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 27.210\ (4)\ \text{\AA}$

$b = 5.2244\ (7)\ \text{\AA}$

$c = 19.007\ (3)\ \text{\AA}$

$\beta = 119.507\ (2)^\circ$

$V = 2351.5\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 1088$

$D_x = 1.485\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2246 reflections

$\theta = 2.5\text{--}23.7^\circ$

$\mu = 1.09\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Block, yellow

$0.32 \times 0.20 \times 0.13\ \text{mm}$

### Data collection

Bruker SMART CCD area detector  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2000)

$T_{\min} = 0.722$ ,  $T_{\max} = 0.871$

6855 measured reflections

2303 independent reflections

2062 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -33 \rightarrow 33$

$k = -6 \rightarrow 6$

$l = -23 \rightarrow 20$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

|                   |  |
|-------------------|--|
| $wR(F^2) = 0.128$ | H-atom parameters constrained                          |
| $S = 1.01$        | $w = 1/[\sigma^2(F_o^2) + (0.0784P)^2 + 2.4971P]$      |
| 2303 reflections  | where $P = (F_o^2 + 2F_c^2)/3$                         |
| 160 parameters    | $(\Delta/\sigma)_{\max} < 0.001$                       |
| 1 restraint       | $\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$  |
|                   | $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$ |

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\text{sigma}(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|     | <i>x</i>      | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|--------------|----------------------------------|
| Zn1 | 0.0000        | 0.78566 (12) | 0.2500       | 0.0427 (3)                       |
| N1  | 0.02638 (12)  | 0.5960 (6)   | 0.18435 (18) | 0.0394 (7)                       |
| O1  | 0.06578 (11)  | 0.9989 (6)   | 0.30670 (18) | 0.0549 (7)                       |
| O2  | 0.24426 (12)  | 1.3537 (7)   | 0.3745 (2)   | 0.0665 (9)                       |
| O3  | -0.03914 (17) | 0.7542 (6)   | 0.0242 (2)   | 0.0729 (10)                      |
| C1  | 0.11535 (15)  | 0.8329 (7)   | 0.2413 (2)   | 0.0403 (8)                       |
| C2  | 0.10942 (14)  | 1.0010 (7)   | 0.2954 (2)   | 0.0402 (8)                       |
| C3  | 0.15270 (16)  | 1.1795 (8)   | 0.3399 (3)   | 0.0465 (9)                       |
| H3  | 0.1490        | 1.2918       | 0.3750       | 0.056*                           |
| C4  | 0.20061 (16)  | 1.1895 (8)   | 0.3319 (3)   | 0.0489 (9)                       |
| C5  | 0.20638 (16)  | 1.0283 (9)   | 0.2781 (3)   | 0.0550 (10)                      |
| H5  | 0.2382        | 1.0385       | 0.2720       | 0.066*                           |
| C6  | 0.16505 (16)  | 0.8560 (9)   | 0.2348 (3)   | 0.0505 (10)                      |
| H6  | 0.1694        | 0.7483       | 0.1993       | 0.061*                           |
| C7  | 0.2397 (2)    | 1.5304 (9)   | 0.4279 (3)   | 0.0675 (13)                      |
| H7A | 0.2080        | 1.6411       | 0.3976       | 0.101*                           |
| H7B | 0.2736        | 1.6309       | 0.4545       | 0.101*                           |
| H7C | 0.2345        | 1.4386       | 0.4675       | 0.101*                           |
| C8  | 0.07515 (15)  | 0.6467 (7)   | 0.1911 (2)   | 0.0417 (8)                       |
| H8  | 0.0851        | 0.5491       | 0.1591       | 0.050*                           |
| C9  | -0.00946 (17) | 0.4112 (8)   | 0.1224 (2)   | 0.0508 (9)                       |
| H9A | -0.0260       | 0.2943       | 0.1446       | 0.061*                           |
| H9B | 0.0134        | 0.3118       | 0.1061       | 0.061*                           |
| C10 | -0.05497 (17) | 0.5418 (8)   | 0.0510 (2)   | 0.0517 (10)                      |
| C11 | -0.1095 (2)   | 0.4911 (15)  | 0.0025 (3)   | 0.0929 (17)                      |

## supplementary materials

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|     |             |             |             |           |
|-----|-------------|-------------|-------------|-----------|
| H11 | -0.1303     | 0.3563      | 0.0065      | 0.111*    |
| C12 | -0.1294 (3) | 0.6947 (16) | -0.0583 (4) | 0.102 (2) |
| H12 | -0.1661     | 0.7157      | -0.1007     | 0.123*    |
| C13 | -0.0861 (3) | 0.8419 (15) | -0.0423 (3) | 0.103 (2) |
| H13 | -0.0874     | 0.9855      | -0.0721     | 0.123*    |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| Zn1 | 0.0333 (4)  | 0.0510 (4)  | 0.0525 (4)  | 0.000        | 0.0278 (3)  | 0.000        |
| N1  | 0.0346 (15) | 0.0452 (16) | 0.0426 (16) | 0.0013 (13)  | 0.0222 (13) | 0.0020 (13)  |
| O1  | 0.0396 (15) | 0.0674 (18) | 0.0709 (18) | -0.0102 (13) | 0.0372 (14) | -0.0200 (15) |
| O2  | 0.0414 (16) | 0.070 (2)   | 0.083 (2)   | -0.0157 (14) | 0.0268 (16) | -0.0085 (18) |
| O3  | 0.079 (2)   | 0.070 (2)   | 0.064 (2)   | 0.0066 (17)  | 0.0316 (19) | 0.0094 (16)  |
| C1  | 0.0326 (18) | 0.047 (2)   | 0.045 (2)   | 0.0031 (15)  | 0.0226 (16) | 0.0047 (16)  |
| C2  | 0.0301 (17) | 0.0457 (19) | 0.047 (2)   | 0.0029 (14)  | 0.0205 (15) | 0.0023 (16)  |
| C3  | 0.038 (2)   | 0.047 (2)   | 0.054 (2)   | -0.0002 (16) | 0.0232 (18) | -0.0007 (17) |
| C4  | 0.0342 (19) | 0.052 (2)   | 0.056 (2)   | -0.0027 (16) | 0.0188 (18) | 0.0068 (18)  |
| C5  | 0.0336 (19) | 0.074 (3)   | 0.066 (3)   | 0.0003 (18)  | 0.0304 (19) | 0.005 (2)    |
| C6  | 0.037 (2)   | 0.065 (3)   | 0.057 (2)   | 0.0034 (18)  | 0.0289 (18) | -0.002 (2)   |
| C7  | 0.059 (3)   | 0.060 (3)   | 0.068 (3)   | -0.018 (2)   | 0.019 (2)   | -0.003 (2)   |
| C8  | 0.0398 (19) | 0.047 (2)   | 0.044 (2)   | 0.0051 (15)  | 0.0252 (17) | 0.0000 (16)  |
| C9  | 0.052 (2)   | 0.045 (2)   | 0.060 (2)   | -0.0084 (18) | 0.031 (2)   | -0.0046 (19) |
| C10 | 0.043 (2)   | 0.065 (3)   | 0.050 (2)   | -0.0058 (18) | 0.0245 (18) | -0.014 (2)   |
| C11 | 0.050 (3)   | 0.155 (5)   | 0.079 (3)   | -0.021 (3)   | 0.036 (3)   | -0.049 (3)   |
| C12 | 0.064 (4)   | 0.167 (7)   | 0.056 (3)   | 0.042 (4)    | 0.015 (3)   | -0.015 (3)   |
| C13 | 0.119 (6)   | 0.113 (5)   | 0.055 (3)   | 0.052 (5)    | 0.027 (4)   | 0.014 (3)    |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|                         |             |          |            |
|-------------------------|-------------|----------|------------|
| Zn1—O1 <sup>i</sup>     | 1.925 (3)   | C4—C5    | 1.391 (6)  |
| Zn1—O1                  | 1.925 (3)   | C5—C6    | 1.357 (6)  |
| Zn1—N1                  | 1.984 (3)   | C5—H5    | 0.9300     |
| Zn1—N1 <sup>i</sup>     | 1.984 (3)   | C6—H6    | 0.9300     |
| N1—C8                   | 1.296 (4)   | C7—H7A   | 0.9600     |
| N1—C9                   | 1.463 (5)   | C7—H7B   | 0.9600     |
| O1—C2                   | 1.306 (4)   | C7—H7C   | 0.9600     |
| O2—C4                   | 1.362 (5)   | C8—H8    | 0.9300     |
| O2—C7                   | 1.422 (6)   | C9—C10   | 1.479 (6)  |
| O3—C13                  | 1.360 (7)   | C9—H9A   | 0.9700     |
| O3—C10                  | 1.375 (5)   | C9—H9B   | 0.9700     |
| C1—C2                   | 1.422 (5)   | C10—C11  | 1.332 (6)  |
| C1—C6                   | 1.422 (5)   | C11—C12  | 1.465 (10) |
| C1—C8                   | 1.423 (5)   | C11—H11  | 0.9300     |
| C2—C3                   | 1.411 (5)   | C12—C13  | 1.311 (11) |
| C3—C4                   | 1.386 (6)   | C12—H12  | 0.9300     |
| C3—H3                   | 0.9300      | C13—H13  | 0.9300     |
| O1 <sup>i</sup> —Zn1—O1 | 109.27 (18) | C1—C6—H6 | 118.6      |

|                                      |             |             |           |
|--------------------------------------|-------------|-------------|-----------|
| O1 <sup>i</sup> —Zn1—N1              | 117.49 (12) | O2—C7—H7A   | 109.5     |
| O1—Zn1—N1                            | 96.69 (11)  | O2—C7—H7B   | 109.5     |
| O1 <sup>i</sup> —Zn1—N1 <sup>i</sup> | 96.69 (11)  | H7A—C7—H7B  | 109.5     |
| O1—Zn1—N1 <sup>i</sup>               | 117.49 (12) | O2—C7—H7C   | 109.5     |
| N1—Zn1—N1 <sup>i</sup>               | 120.08 (18) | H7A—C7—H7C  | 109.5     |
| C8—N1—C9                             | 117.3 (3)   | H7B—C7—H7C  | 109.5     |
| C8—N1—Zn1                            | 120.4 (3)   | N1—C8—C1    | 128.1 (3) |
| C9—N1—Zn1                            | 122.1 (2)   | N1—C8—H8    | 115.9     |
| C2—O1—Zn1                            | 125.6 (2)   | C1—C8—H8    | 115.9     |
| C4—O2—C7                             | 118.4 (3)   | N1—C9—C10   | 111.1 (3) |
| C13—O3—C10                           | 107.1 (5)   | N1—C9—H9A   | 109.4     |
| C2—C1—C6                             | 117.5 (3)   | C10—C9—H9A  | 109.4     |
| C2—C1—C8                             | 125.7 (3)   | N1—C9—H9B   | 109.4     |
| C6—C1—C8                             | 116.7 (3)   | C10—C9—H9B  | 109.4     |
| O1—C2—C3                             | 117.7 (3)   | H9A—C9—H9B  | 108.0     |
| O1—C2—C1                             | 123.4 (3)   | C11—C10—O3  | 110.5 (5) |
| C3—C2—C1                             | 118.9 (3)   | C11—C10—C9  | 133.4 (5) |
| C4—C3—C2                             | 120.8 (4)   | O3—C10—C9   | 116.0 (4) |
| C4—C3—H3                             | 119.6       | C10—C11—C12 | 104.7 (6) |
| C2—C3—H3                             | 119.6       | C10—C11—H11 | 127.6     |
| O2—C4—C3                             | 123.4 (4)   | C12—C11—H11 | 127.6     |
| O2—C4—C5                             | 115.9 (4)   | C13—C12—C11 | 107.5 (5) |
| C3—C4—C5                             | 120.7 (4)   | C13—C12—H12 | 126.2     |
| C6—C5—C4                             | 119.2 (3)   | C11—C12—H12 | 126.2     |
| C6—C5—H5                             | 120.4       | C12—C13—O3  | 110.1 (7) |
| C4—C5—H5                             | 120.4       | C12—C13—H13 | 124.9     |
| C5—C6—C1                             | 122.9 (4)   | O3—C13—H13  | 124.9     |
| C5—C6—H6                             | 118.6       |             |           |

Symmetry codes: (i)  $-x, y, -z+1/2$ .

*Hydrogen-bond geometry* (Å, °)

| <i>D</i> —H··· <i>A</i>   | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| C9—H9A···O1 <sup>ii</sup> | 0.97        | 2.32          | 3.292 (6)             | 177                     |

Symmetry codes: (ii)  $-x, y-1, -z+1/2$ .

Fig. 1

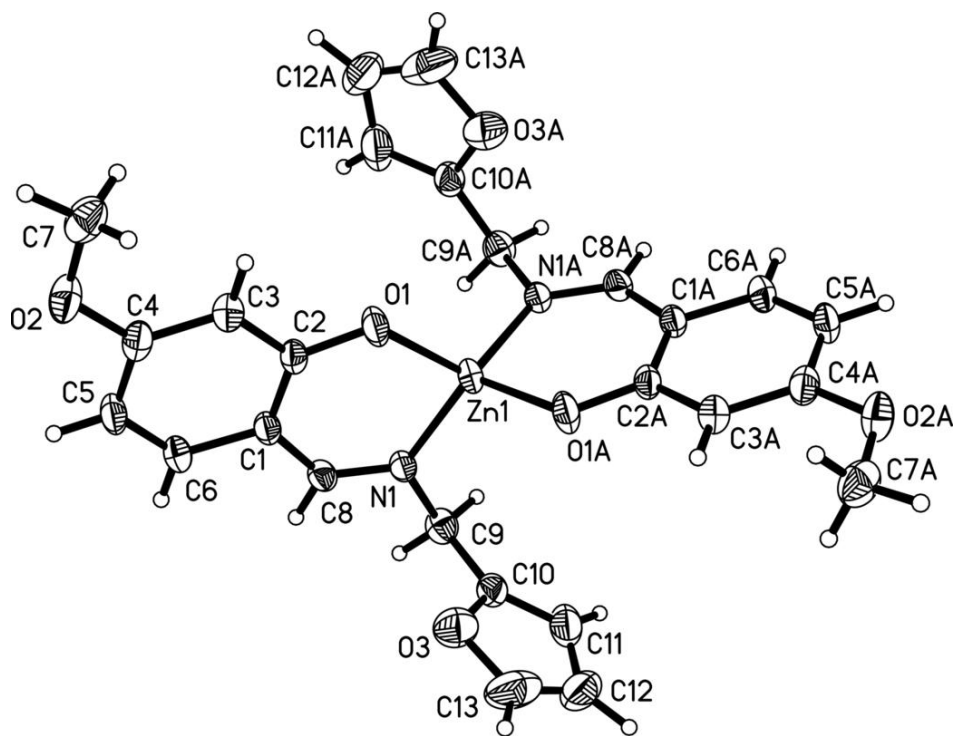




Fig. 2

