

Bis[2-(2-aminoethyl)-1H-benzimidazole- κ^2N^2,N^3]zinc(II) bis(perchlorate)

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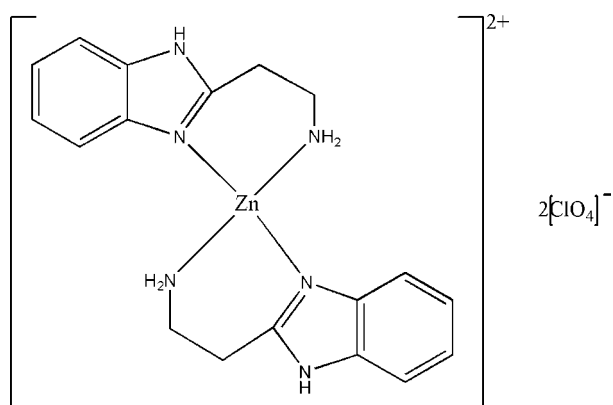
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.008$ Å; disorder in main residue; R factor = 0.066; wR factor = 0.184; data-to-parameter ratio = 12.4.

In the title compound, $[Zn(C_9H_{11}N_3)_2](ClO_4)_2$, the Zn^{II} atom resides on a crystallographic twofold axis and is coordinated by two benzimidazole N [$Zn \cdots N = 1.993$ (4) Å] and two amine N atoms [$Zn \cdots N = 2.036$ (4) Å] in a distorted tetrahedral geometry. The crystal packing is dominated by $N-H \cdots O$ interactions involving the perchlorate anions and $\pi-\pi$ stacking interactions with an interplanar separation of 3.42 Å. A weak $C-H \cdots O$ interaction is also present.

Related literature

For related literature, see: Cescon & Day (1961); Maurva *et al.* (2006); Qiu & Tong (2005); Vallee & Auld (1990).



Experimental

Crystal data

$[Zn(C_9H_{11}N_3)_2](ClO_4)_2$
 $M_r = 586.69$
Monoclinic, $C2/c$
 $a = 11.150$ (3) Å
 $b = 15.343$ (4) Å
 $c = 14.156$ (4) Å
 $\beta = 93.322$ (4)°

$V = 2417.7$ (12) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.29$ mm⁻¹
 $T = 293$ (2) K
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector
diffractometer
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.698$, $T_{max} = 0.782$

5777 measured reflections
2131 independent reflections
1880 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.184$
 $S = 1.10$
2131 reflections
172 parameters

15 restraints
H-atom parameters constrained
 $\Delta\rho_{max} = 0.81$ e Å⁻³
 $\Delta\rho_{min} = -0.47$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2A \cdots O1$	0.86	2.09	2.946 (6)	174
$N3-H3A \cdots O4^i$	0.90	2.12	2.953 (15)	154
$C8-H8A \cdots O1^{ii}$	0.97	2.42	3.210 (9)	138

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); 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: GG2058).

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supplementary materials

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Bis[2-(2-aminoethyl)-1*H*-benzimidazole- κ^2 N²,N³]zinc(II) bis(perchlorate)

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Comment

Benzimidazole is of considerable interest as a ligand for transition metal ions. The complexes of transition metal salts with benzimidazole derivatives have been extensively studied as models of some important biological molecules (Maurva *et al.*, 2006). Incorporation of a benzimidazole moiety into alpha-amino acid molecules appeared to be of interest since the benzimidazole group has known biological activity, and its attachment to a carrier group such as an amino acid can facilitate this activity (Cescon & Day, 1961). Zinc complexes may be found in numerous biological systems. They function not only as catalytic centres in enzymes, but also as structural elements supporting three-dimensional protein structures (Vallee & Auld, 1990). In the present paper, we report the synthesis and crystal structure of a new zinc(II) benzimidazole complex, the title compound.

In (I), the Zn(II) ion exhibits a distorted tetrahedral geometry. The coordination sphere of the Zn(II) ion is comprised with two benzimidazole N atoms and two amine N atoms. The Zn—N bond distances (Table 1) are different from those reported in the literature. The Zn—N1 bond distance of 1.993 (4) Å is smaller than that reported in the literature (Qiu & Tong, 2005). The N1—Zn—N3 and N1—Zn—N3A (symmetry code: A -x + 2,y,-z + 1/2) bond angles are 97.02 (16)° and 118.10 (17)°, respectively, indicating a distortion of the tetrahedral coordination.

The ellipsoid plot of the molecule is shown in Fig. 1. The crystal structure of (I) is composed of Bis(1*H*-2-aminoethylbenzimidazole)zinc(II) cations and perchlorate anions. As illustrated in Fig. 2, intramolecular N—H···O hydrogen bonds and π ··· π stacking interactions between the benzene ring and imidazole ring [$Cg1 \cdots Cg2(1/2 - x, 1/2 - y, 1 - z) = 3.7296$ Å; $Cg1$ is the centroid of atoms N1, C1, C6, N2, C7, $Cg2$ is the centroid of atoms C1—C6] play key roles in stabilizing the crystal packing. The detailed hydrogen bonds information are listed in Table 2.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification.

The title compound was prepared by adding a methanol solution (5 ml) of Zn(ClO₄)₂·6H₂O (0.5 mmol) to a methanol solution (10 ml) of 2-aminoethylbenzimidazole dihydrochloride (0.5 mmol) (Cescon & Day, 1961) neutralized by potassium carbonate. The mixture was stirred for about four hours and then filtered. Afterwards, the filtrate was slowly evaporated at room temperature to yield colorless crystals of (I) suitable for X-ray analysis. Elemental analyses of the title compound found: C 36.86%, H 3.75%, N 14.33%, and the components of the compound are calculated as C 36.85%, H 3.79%, N 14.30%.

Refinement

Disorder is present in the perchlorate anion and aminoethyl bridge and was modelled successfully. H atoms were placed in calculated positions and included in the refinement in the riding-model approximation, with C—H distances in the range 0.93–0.97 Å, N—H distances in the range 0.86–0.90 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom.

Figures

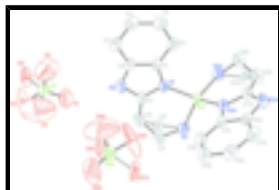


Fig. 1. The structure of the title compound with 30% displacement ellipsoids. H atoms have been omitted for clarity.

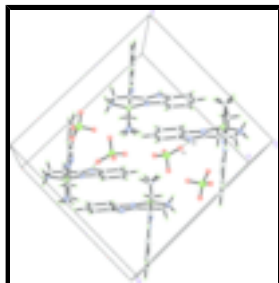


Fig. 2. The packing diagram of (I) with N—H...O hydrogen bonds shown as dashed lines.

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Crystal data

$[\text{Zn}(\text{C}_9\text{H}_{11}\text{N}_3)_2](\text{ClO}_4)_2$

$M_r = 586.69$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 11.150\ (3)\ \text{\AA}$

$b = 15.343\ (4)\ \text{\AA}$

$c = 14.156\ (4)\ \text{\AA}$

$\beta = 93.322\ (4)^\circ$

$V = 2417.7\ (12)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1200$

$D_x = 1.612\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1957 reflections

$\theta = 2.3\text{--}23.9^\circ$

$\mu = 1.29\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Block, colorless

$0.30 \times 0.20 \times 0.20\ \text{mm}$

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ (2)\ \text{K}$

2131 independent reflections

1880 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 25.0^\circ$

φ and ω scans $\theta_{\min} = 2.3^\circ$
 Absorption correction: multi-scan $h = -13 \rightarrow 13$
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.698$, $T_{\max} = 0.782$ $k = -18 \rightarrow 18$
 5777 measured reflections $l = -10 \rightarrow 16$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.066$ H-atom parameters constrained
 $wR(F^2) = 0.184$ $w = 1/[\sigma^2(F_o^2) + (0.1191P)^2 + 1.6906P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.10$ $(\Delta/\sigma)_{\max} < 0.001$
 2131 reflections $\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$
 172 parameters $\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$
 15 restraints Extinction correction: none
 Primary atom site location: structure-invariant direct methods

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	1.0000	0.13946 (4)	0.2500	0.0506 (3)	
N1	0.8741 (3)	0.2124 (2)	0.1829 (3)	0.0534 (9)	
N2	0.6929 (3)	0.2674 (3)	0.1500 (3)	0.0655 (11)	
H2A	0.6165	0.2745	0.1504	0.079*	
C1	0.8843 (4)	0.2811 (3)	0.1191 (3)	0.0538 (11)	
C2	0.9833 (5)	0.3136 (4)	0.0754 (4)	0.0712 (14)	
H2	1.0595	0.2900	0.0872	0.085*	
C3	0.9638 (6)	0.3819 (4)	0.0142 (5)	0.0805 (16)	
H3	1.0287	0.4055	-0.0155	0.097*	
C4	0.8497 (6)	0.4174 (4)	-0.0050 (4)	0.0776 (16)	
H4	0.8413	0.4643	-0.0464	0.093*	
C5	0.7494 (6)	0.3855 (3)	0.0351 (4)	0.0686 (14)	

supplementary materials

H5	0.6732	0.4083	0.0211	0.082*	
C6	0.7700 (4)	0.3157 (3)	0.0990 (3)	0.0549 (11)	
C7	0.7577 (4)	0.2068 (3)	0.1993 (4)	0.0624 (12)	
C8	0.7035 (6)	0.1424 (4)	0.2624 (5)	0.0905 (17)	
H8A	0.6298	0.1675	0.2837	0.109*	0.594 (12)
H8B	0.6812	0.0916	0.2247	0.109*	0.594 (12)
H8A'	0.6876	0.1728	0.3205	0.109*	0.406 (12)
H8B'	0.6261	0.1264	0.2327	0.109*	0.406 (12)
Cl1	0.37395 (13)	0.37873 (10)	0.10975 (10)	0.0736 (4)	
O1	0.4321 (5)	0.2999 (4)	0.1393 (6)	0.141 (2)	
N3	0.8879 (4)	0.0694 (3)	0.3295 (3)	0.0673 (11)	
H3A	0.8725	0.0179	0.3008	0.081*	0.594 (12)
H3B	0.9256	0.0584	0.3861	0.081*	0.594 (12)
H3A'	0.9179	0.0152	0.3372	0.081*	0.406 (12)
H3B'	0.8869	0.0940	0.3871	0.081*	0.406 (12)
O2	0.4361 (8)	0.4352 (7)	0.0603 (7)	0.214 (5)	
O3	0.2643 (9)	0.3764 (10)	0.130 (2)	0.235 (14)	0.594 (12)
C9	0.7735 (7)	0.1132 (8)	0.3445 (6)	0.0905 (17)	0.594 (12)
H9A	0.7243	0.0735	0.3790	0.109*	0.594 (12)
H9B	0.7904	0.1633	0.3849	0.109*	0.594 (12)
O3'	0.2863 (12)	0.3531 (10)	0.0330 (13)	0.118 (6)	0.406 (12)
C9'	0.7639 (7)	0.0630 (5)	0.2892 (9)	0.061 (4)	0.406 (12)
H9A'	0.7642	0.0260	0.2337	0.073*	0.406 (12)
H9B'	0.7167	0.0335	0.3350	0.073*	0.406 (12)
O4	0.364 (2)	0.4319 (9)	0.1837 (10)	0.337 (9)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0418 (4)	0.0565 (5)	0.0526 (5)	0.000	-0.0053 (3)	0.000
N1	0.0406 (19)	0.056 (2)	0.063 (2)	0.0001 (15)	-0.0033 (16)	0.0050 (17)
N2	0.0411 (19)	0.069 (2)	0.086 (3)	0.0064 (18)	0.0020 (19)	0.003 (2)
C1	0.050 (2)	0.051 (2)	0.060 (3)	-0.0044 (18)	-0.009 (2)	-0.004 (2)
C2	0.057 (3)	0.076 (3)	0.080 (4)	-0.005 (2)	-0.002 (3)	0.015 (3)
C3	0.076 (4)	0.074 (3)	0.092 (4)	-0.009 (3)	0.005 (3)	0.026 (3)
C4	0.094 (4)	0.062 (3)	0.075 (4)	0.001 (3)	-0.010 (3)	0.012 (3)
C5	0.077 (4)	0.053 (2)	0.074 (3)	0.008 (2)	-0.019 (3)	-0.003 (2)
C6	0.054 (3)	0.047 (2)	0.062 (3)	0.0038 (19)	-0.009 (2)	-0.009 (2)
C7	0.044 (2)	0.063 (3)	0.080 (3)	0.001 (2)	-0.001 (2)	0.012 (2)
C8	0.061 (3)	0.099 (3)	0.113 (4)	0.001 (2)	0.019 (3)	0.030 (3)
Cl1	0.0667 (9)	0.0818 (9)	0.0722 (9)	0.0043 (6)	0.0054 (7)	0.0076 (7)
O1	0.095 (4)	0.146 (5)	0.182 (6)	0.024 (4)	0.007 (4)	0.039 (4)
N3	0.064 (2)	0.073 (3)	0.065 (2)	-0.004 (2)	0.005 (2)	0.014 (2)
O2	0.172 (7)	0.230 (9)	0.236 (9)	-0.102 (7)	-0.023 (7)	0.106 (8)
O3	0.056 (6)	0.149 (11)	0.51 (4)	0.036 (6)	0.073 (12)	0.136 (18)
C9	0.061 (3)	0.099 (3)	0.113 (4)	0.001 (2)	0.019 (3)	0.030 (3)
O3'	0.048 (7)	0.149 (13)	0.152 (14)	0.004 (6)	-0.036 (7)	-0.047 (10)
C9'	0.055 (7)	0.056 (7)	0.072 (8)	-0.012 (5)	0.009 (6)	0.012 (6)

O4 0.57 (3) 0.241 (13) 0.207 (10) -0.006 (16) 0.084 (15) -0.121 (10)

Geometric parameters (Å, °)

Zn1—N1 ⁱ	1.993 (4)	C8—H8A	0.9700
Zn1—N1	1.993 (4)	C8—H8B	0.9700
Zn1—N3 ⁱ	2.036 (4)	C8—H8A'	0.9700
Zn1—N3	2.036 (4)	C8—H8B'	0.9700
N1—C7	1.335 (6)	C3—H3	0.9300
N1—C1	1.397 (6)	C11—O3	1.273 (10)
C5—C4	1.373 (9)	C11—O2	1.333 (7)
C5—C6	1.412 (7)	C11—O4	1.336 (10)
C5—H5	0.9300	C11—O1	1.423 (6)
C1—C2	1.389 (7)	C11—O3'	1.472 (12)
C1—C6	1.394 (6)	N3—C9'	1.468 (8)
C7—N2	1.347 (6)	N3—C9	1.468 (8)
C7—C8	1.484 (7)	N3—H3A	0.9000
C6—N2	1.372 (6)	N3—H3B	0.9000
N2—H2A	0.8600	N3—H3A'	0.9000
C2—C3	1.369 (8)	N3—H3B'	0.9000
C2—H2	0.9300	C9—H9A	0.9700
C4—C3	1.396 (8)	C9—H9B	0.9700
C4—H4	0.9300	C9'—H9A'	0.9700
C8—C9'	1.433 (7)	C9'—H9B'	0.9700
C8—C9	1.433 (7)		
N1 ⁱ —Zn1—N1	111.6 (2)	H8A—C8—H8B'	59.1
N1 ⁱ —Zn1—N3 ⁱ	97.02 (16)	H8B—C8—H8B'	50.4
N1—Zn1—N3 ⁱ	118.10 (17)	H8A'—C8—H8B'	106.7
N1 ⁱ —Zn1—N3	118.10 (17)	C2—C3—C4	122.1 (5)
N1—Zn1—N3	97.02 (16)	C2—C3—H3	119.0
N3 ⁱ —Zn1—N3	116.3 (3)	C4—C3—H3	119.0
C7—N1—C1	106.1 (4)	O3—C11—O2	132.2 (7)
C7—N1—Zn1	123.1 (3)	O3—C11—O4	73.4 (14)
C1—N1—Zn1	130.6 (3)	O2—C11—O4	94.9 (10)
C4—C5—C6	115.4 (5)	O3—C11—O1	109.7 (6)
C4—C5—H5	122.3	O2—C11—O1	117.7 (6)
C6—C5—H5	122.3	O4—C11—O1	110.3 (9)
C2—C1—C6	120.9 (4)	O3—C11—O3'	63.5 (13)
C2—C1—N1	130.9 (4)	O2—C11—O3'	97.4 (9)
C6—C1—N1	108.2 (4)	O4—C11—O3'	131.1 (11)
N1—C7—N2	111.3 (4)	O1—C11—O3'	105.2 (7)
N1—C7—C8	125.6 (4)	C9'—N3—Zn1	114.5 (5)
N2—C7—C8	123.1 (4)	C9—N3—Zn1	113.9 (5)
N2—C6—C1	106.2 (4)	C9'—N3—H3A	67.4
N2—C6—C5	131.6 (5)	C9—N3—H3A	108.8
C1—C6—C5	122.2 (5)	Zn1—N3—H3A	108.8
C7—N2—C6	108.2 (4)	C9'—N3—H3B	135.6

supplementary materials

C7—N2—H2A	125.9	C9—N3—H3B	108.8
C6—N2—H2A	125.9	Zn1—N3—H3B	108.8
C3—C2—C1	117.1 (5)	H3A—N3—H3B	107.7
C3—C2—H2	121.5	C9'—N3—H3A'	108.6
C1—C2—H2	121.5	C9—N3—H3A'	136.4
C5—C4—C3	122.4 (5)	Zn1—N3—H3A'	108.6
C5—C4—H4	118.8	H3A—N3—H3A'	45.8
C3—C4—H4	118.8	H3B—N3—H3A'	64.4
C9'—C8—C9	45.1 (7)	C9'—N3—H3B'	108.6
C9'—C8—C7	121.6 (6)	C9—N3—H3B'	67.7
C9—C8—C7	118.3 (6)	Zn1—N3—H3B'	108.6
C9'—C8—H8A	130.4	H3A—N3—H3B'	139.9
C9—C8—H8A	107.7	H3B—N3—H3B'	45.6
C7—C8—H8A	107.7	H3A'—N3—H3B'	107.6
C9'—C8—H8B	64.1	C8—C9—N3	117.6 (6)
C9—C8—H8B	107.7	C8—C9—H9A	107.9
C7—C8—H8B	107.7	N3—C9—H9A	107.9
H8A—C8—H8B	107.1	C8—C9—H9B	107.9
C9'—C8—H8A'	106.9	N3—C9—H9B	107.9
C9—C8—H8A'	65.3	H9A—C9—H9B	107.2
C7—C8—H8A'	106.9	C8—C9'—N3	117.6 (6)
H8A—C8—H8A'	49.3	C8—C9'—H9A'	107.9
H8B—C8—H8A'	143.1	N3—C9'—H9A'	107.9
C9'—C8—H8B'	106.9	C8—C9'—H9B'	107.9
C9—C8—H8B'	134.5	N3—C9'—H9B'	107.9
C7—C8—H8B'	106.9	H9A'—C9'—H9B'	107.2

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots O1	0.86	2.09	2.946 (6)	174
N3—H3A \cdots O4 ⁱⁱ	0.90	2.12	2.953 (15)	154
C8—H8A \cdots O1 ⁱⁱⁱ	0.97	2.42	3.210 (9)	138

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

Fig. 1

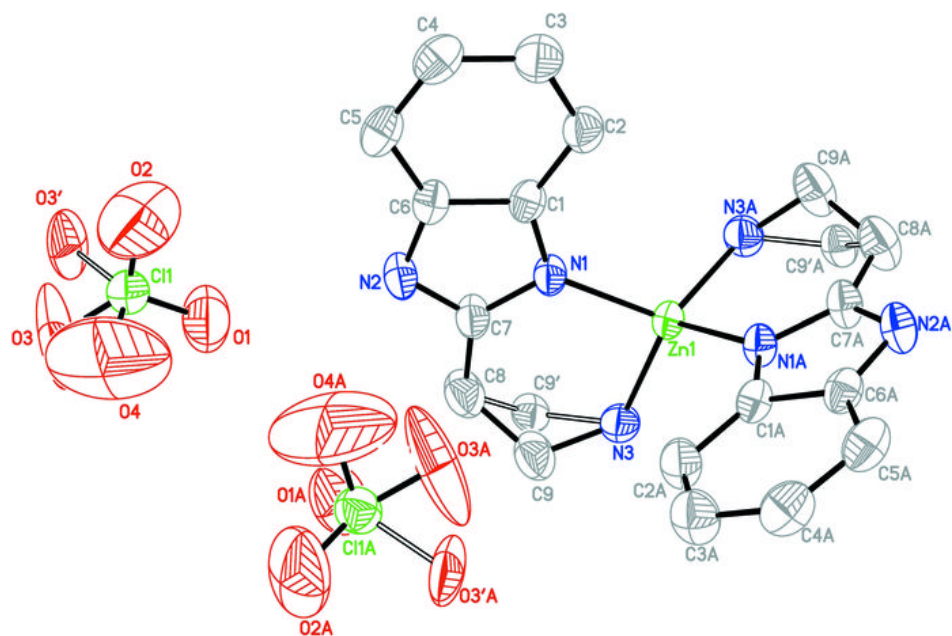


Fig. 2

