

# Structural characterization of two benzene-1,2-diamine complexes of zinc chloride: a molecular compound and a co-crystal salt

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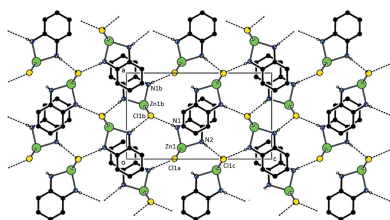
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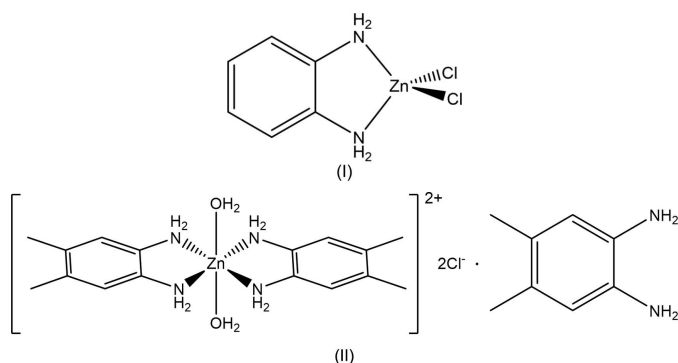
The structures of two zinc complexes containing bidentate benzene-1,2-diamine ligands are reported. (Benzene-1,2-diamine- $\kappa^2N,N'$ )dichloridozinc,  $[\text{ZnCl}_2(\text{C}_6\text{H}_8\text{N}_2)]$ , (I), displays a distorted tetrahedral coordination sphere for the metal cation. The diamine ligand and the Zn atom reside on a crystallographic mirror plane. In the 1:1 co-crystal salt *trans*-diaquabis(4,5-dimethylbenzene-1,2-diamine- $\kappa^2N,N'$ )zinc chloride-4,5-dimethylbenzene-1,2-diamine (1/1),  $[\text{Zn}(\text{C}_8\text{H}_{12}\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 2\text{C}_8\text{H}_{12}\text{N}_2$ , (II), the zinc(II) complex cation exhibits a tetragonally distorted octahedral coordination sphere. The Zn atom sits on a crystallographically imposed inversion center and the diamine ligands are tilted  $30.63(6)^\circ$  with respect to the  $\text{ZnN}_4$  plane. Both complexes exhibit extensive hydrogen bonding. In (I), a stacked-sheet extended structure parallel to (101) is observed. In (II), the co-crystallized diamine is hydrogen-bonded to the complex cation *via*  $\text{O}-\text{H} \cdots \text{N}$  and  $\text{N}-\text{H} \cdots \text{N}$  linkages. These units are in turn linked into planes along (200) by  $\text{O}-\text{H} \cdots \text{Cl}$  and  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bonds.

## 1. Chemical context

Zinc complexes bearing aryl diimine and/or heterocyclic ligands have been shown to emit brightly in the blue region of the spectrum (DeStefano & Geiger, 2016; Tan *et al.*, 2012; Liu *et al.*, 2010; Xu *et al.*, 2008; Yue *et al.*, 2006; Singh *et al.*, 2011; Wang *et al.*, 2010). These complexes have potential use in photooptical devices because of their high thermal stability and the ability to tune their color by varying ancillary ligands and coordination geometry (Xu *et al.*, 2008). Most of the compounds explored have acetate ligands. Substituting acetate with halide ligands provides an avenue for modulating the electronic structure of the complex and, hence, the carrier transport character. Toward that end, we have characterized several zinc complexes possessing benzene-1,2-diamine ligands (Geiger, 2012; Geiger & Parsons, 2014) and substituted benzimidazole ligands (DeStefano & Geiger, 2016). The benzene-1,2-diamine-containing complexes previously reported have a monodentate diamine coordination mode. We report herein two new zinc complexes containing bidentate benzene-1,2-diamine ligands: (benzene-1,2-diamine- $\kappa^2N,N'$ )-dichloridozinc, (I), and the 1:1 co-crystal salt *trans*-diaquabis(4,5-dimethylbenzene-1,2-diamine- $\kappa^2N,N'$ )zinc chloride 4,5-dimethylbenzene-1,2-diamine, (II).



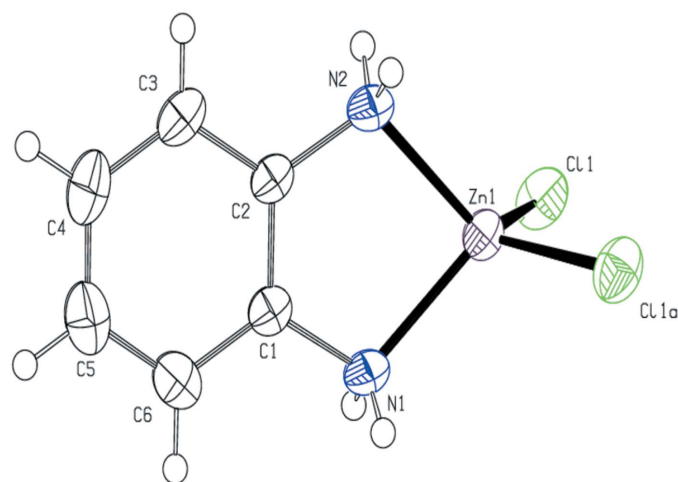
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## 2. Structural commentary

As seen in Fig. 1, compound (I) exhibits a distorted tetrahedral coordination sphere for the metal cation. Tables 1 and 2 give relevant geometric parameters found in the coordination sphere. The diamine ligand and the Zn atom sit on a mirror plane and, hence, are rigorously planar as a result of the symmetry constraint. The Zn–N bond lengths observed at the two temperatures are the same within the calculated s.u. The Zn–Cl bond lengths differ within the s.u., with the 200 K structure being 0.0030 (5) Å longer. The bond lengths observed at both temperatures fall within the s.u. of the average value [2.221 (19) Å] of similar complexes but the Cl–Zn–Cl bond angles are smaller than the average of the values [115 (1)°] reported for similar Zn<sup>II</sup> dichlorides in a tetrahedral environment (Shi *et al.*, 2010; You, 2005; Lee *et al.*, 2007).

Compound (II) consists of a Zn<sup>II</sup> complex cation with two bidentate 4,5-dimethylbenzene-1,2-diamine ligands and *trans* water ligands, chloride counter-ions and a non-coordinating molecule of 4,5-dimethylbenzene-1,2-diamine. The compound is thus classified as a co-crystal salt (Grothe *et al.*, 2016). A representation of (II) is found in Fig. 2. The Zn<sup>II</sup> ion sits on a crystallographically imposed center of symmetry and has a



**Figure 1**  
The molecular structure of (Ia), showing the atom-labeling scheme. Anisotropic displacement parameters are drawn at the 50% probability level. [Symmetry code: (a)  $x, -y + \frac{3}{2}, z$ .]

**Table 1**  
Selected geometric parameters (Å, °) for (Ia).

Zn1–Cl1	2.2271 (5)	Zn1–N2	2.0454 (18)
Zn1–N1	2.0449 (19)		
Cl1–Zn1–Cl1 <sup>i</sup>	110.82 (2)	N1–Zn1–Cl1	113.82 (3)
N1–Zn1–N2	85.53 (8)	N2–Zn1–Cl1	115.42 (3)

Symmetry code: (i)  $x, -y + \frac{3}{2}, z$ .

**Table 2**  
Selected geometric parameters (Å, °) for (Ib).

Zn1–Cl1	2.2301 (5)	Zn1–N2	2.045 (3)
Zn1–N1	2.047 (2)		
Cl1–Zn1–Cl1 <sup>i</sup>	110.70 (3)	N1–Zn1–Cl1	113.89 (4)
N1–Zn1–N2	85.45 (10)	N2–Zn1–Cl1	115.46 (3)

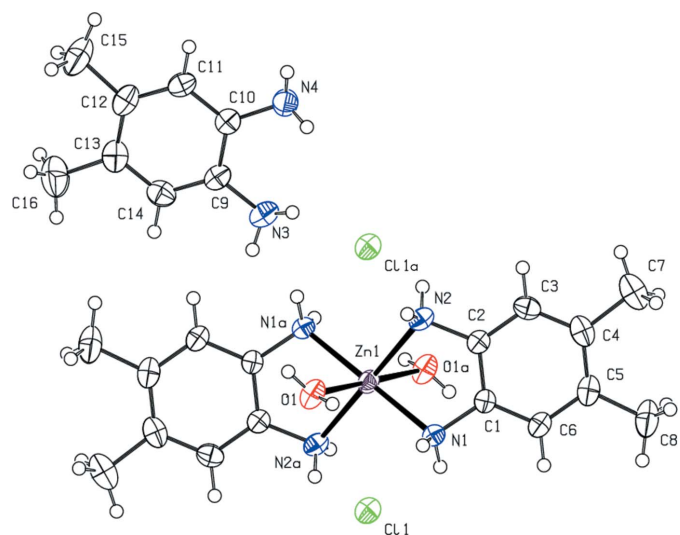
Symmetry code: (i)  $x, -y + \frac{3}{2}, z$ .

**Table 3**  
Selected geometric parameters (Å, °) for (II).

Zn1–N1	2.1214 (15)	Zn1–O1	2.2410 (15)
Zn1–N2	2.1442 (17)		
N1 <sup>i</sup> –Zn1–N2	100.31 (6)	N1–Zn1–O1	92.18 (7)
N1–Zn1–N2	79.69 (6)	N2–Zn1–O1	93.22 (7)

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

tetragonally distorted octahedral coordination geometry. The observed Zn–O bond length (Table 3) is significantly longer than the average of the values [2.14 (3) Å] reported for similar *trans* aqua zinc(II) complexes (Necefoglu *et al.*, 2001; İbrahim *et al.*, 2006; Karimnejad *et al.*, 2011; Gallardo *et al.*, 2008; Li *et al.*, 2012) and the range [2.008 (3) to 2.147 (3) Å] found in the hexaaquazinc(II) cation (Lian *et al.*, 2009). However, it is close to the 2.2057 (16) Å found in the similar cation of *trans*-di-aquabis(cyclohexane-1,2-diamine)zinc dichloride (Karimnejad *et al.*, 2011). The plane of the 4,5-dimethylbenzene-1,2-



**Figure 2**  
The molecular structure of (II) showing the atom-labeling scheme. Anisotropic displacement parameters are drawn at the 50% probability level. [Symmetry code: (a)  $-x + 1, -y + 1, -z + 1$ .]

**Table 4**  
Hydrogen-bond geometry (Å, °) for (Ia).

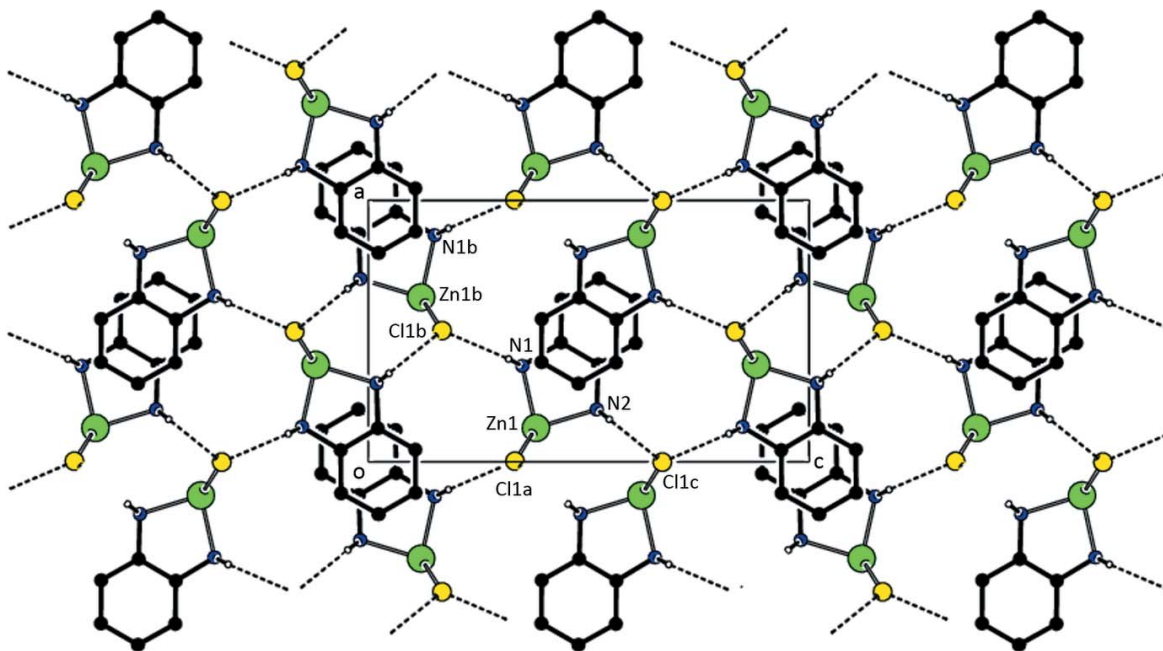
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···Cl1 <sup>ii</sup>	0.86 (2)	2.59 (2)	3.3618 (16)	150.7 (18)
N2–H2···Cl1 <sup>iii</sup>	0.85 (2)	2.52 (2)	3.3204 (16)	157 (2)

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

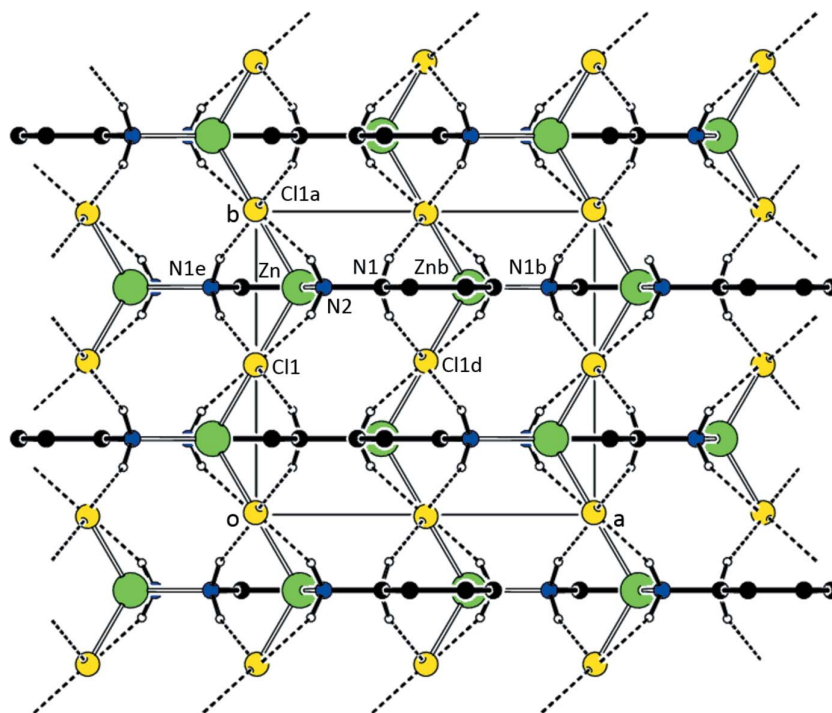
**Table 5**  
Hydrogen-bond geometry (Å, °) for (Ib).

<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>
N1–H1···Cl1 <sup>ii</sup>	0.83 (3)	2.61 (3)	3.368 (2)	152 (2)
N2–H2···Cl1 <sup>iii</sup>	0.83 (3)	2.53 (3)	3.327 (2)	160 (2)

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



**Figure 3**  
A view of the parallel sheets found in (I). Only H atoms involved in the N–H···Cl interactions are shown. [Symmetry codes: (a)  $x, -y + \frac{3}{2}, z$ ; (b)  $x + \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$ ; (c)  $-x, -y + 1, -z + 1$ .]



**Figure 4**  
A view of the parallel sheets found in (I). Only H atoms involved in the N–H···Cl interactions are shown. [Symmetry codes: (a)  $x, -y + \frac{3}{2}, z$ ; (b)  $x + \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$ ; (d)  $x + \frac{1}{2}, y, -z + \frac{1}{2}$ ; (e)  $x - \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$ .]

**Table 6**  
 Hydrogen-bond geometry (Å, °) for (II).

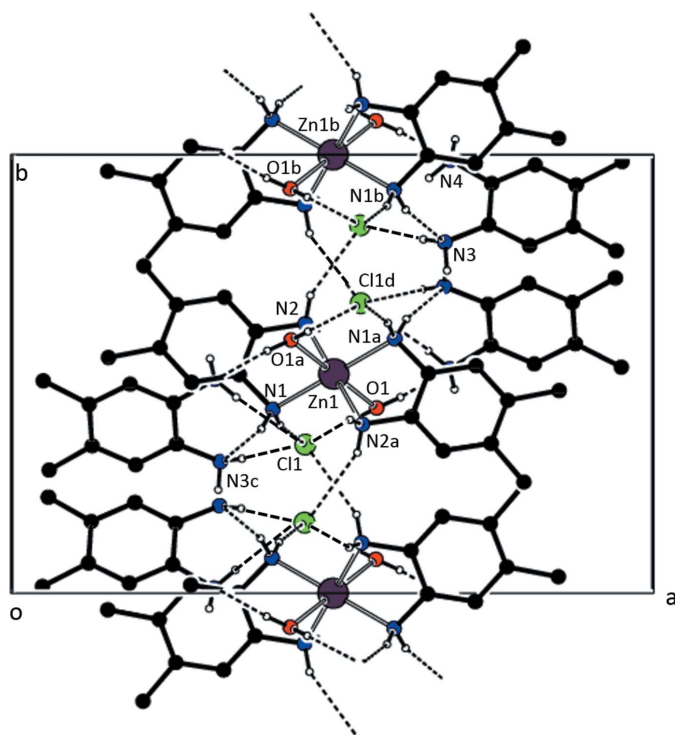
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1WA $\cdots$ N4 <sup>ii</sup>	0.81 (3)	2.13 (3)	2.924 (3)	164 (2)
O1—H1WB $\cdots$ Cl <sup>iii</sup>	0.80 (3)	2.31 (3)	3.1083 (17)	173 (2)
N1—H1A $\cdots$ Cl <sup>iii</sup>	0.84 (2)	2.55 (2)	3.3551 (18)	160.3 (18)
N1—H1B $\cdots$ N3 <sup>iv</sup>	0.85 (2)	2.31 (2)	3.137 (3)	162.6 (18)
N2—H2A $\cdots$ Cl <sup>v</sup>	0.87 (2)	2.63 (2)	3.4401 (19)	155.3 (18)
N2—H2B $\cdots$ Cl <sup>i</sup>	0.81 (2)	2.57 (2)	3.3105 (18)	154 (2)
N3—H3A $\cdots$ Cl <sup>v</sup>	0.84 (3)	2.68 (3)	3.516 (2)	174 (2)
N3—H3B $\cdots$ Cl <sup>vi</sup>	0.87 (3)	2.89 (2)	3.3284 (19)	112.9 (18)
N4—H4B $\cdots$ Cl <sup>v</sup>	0.87 (3)	2.50 (3)	3.355 (2)	171 (2)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+\frac{3}{2}, z-\frac{1}{2}$ ; (iii)  $x, y, z-1$ ; (iv)  $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (v)  $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$ ; (vi)  $-x+1, -y+1, -z+2$ .

diamine ligand is canted 30.63 (6) Å out of the ZnN<sub>4</sub> coordination plane. The nitrogen atoms of the diamine ligand are 0.022 (3) and 0.131 (3) Å out of the benzene plane for N1 and N2, respectively. For the co-crystallized diamine, N3 and N4 are 0.139 (3) and 0.088 (3) Å out of the plane, respectively.

### 3. Supramolecular features

As seen in Figs. 3 and 4 and Tables 4 and 5, N1—H1 $\cdots$ Cl hydrogen bonds between adjacent molecules result in strips of molecules of (I) along [100]. The strips form planes parallel to (101). Additional N2—H2 $\cdots$ Cl bonds join the strips to form the three-dimensional network.



**Figure 5**  
 A view of the hydrogen-bonded network of (II) resulting in slabs along (200). Only H atoms bonded to the nitrogen atoms are shown. [Symmetry codes: (a)  $-x+1, -y+1, -z+1$ ; (b)  $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$ ; (c)  $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (d)  $-x+1, -y+1, -z+2$ .]

Fig. 5 presents a view of the hydrogen-bonding network in (II). N—H $\cdots$ N and O—H $\cdots$ N hydrogen bonds connect inversion-related co-crystallized 4,5-dimethylbenzene-1,2-diamine molecules to the complex cation (see Table 6). Additional N—H $\cdots$ Cl and O—H $\cdots$ Cl hydrogen bonds join the units, forming planes parallel to (200).

### 4. Database survey

The structures of the tetrahedral complexes bis(acetato- $\kappa$ O)(benzene-1,2-diamine- $\kappa$ N)zinc (Mei *et al.*, 2009) and bis(acetato- $\kappa$ O)(4,5-dimethylbenzene-1,2-diamine- $\kappa$ N)zinc (Geiger, 2012) have been reported. Poly[[tris( $\mu_2$ -acetato- $\kappa^2$ O:O')](4-chlorobenzene-1,2-diamine- $\kappa$ N)( $\mu_3$ -hydroxido)-dizinc] ethanol monosolvate] exhibits alternating octahedral and tetrahedral zinc coordination modes (Geiger & Parsons, 2014). Dichlorido[*N*-(2-pyridylmethylidene)benzene-1,4-diamine]zinc has a tetrahedral coordination sphere with intermolecular N—H $\cdots$ Cl hydrogen bonds (Shi *et al.*, 2010). Dichlorido[*N,N,N',N'*-tetramethylcyclohexane-1,2-diamine- $\kappa^2$ N, $N'$ ]zinc displays a tetrahedral coordination geometry (Lee *et al.*, 2007). For examples of zinc complexes with the metal in octahedral coordination including *trans* water ligands, see Ibrahim *et al.* (2006); Necefoglu *et al.* (2001); Karimnejad *et al.* (2011). A tetragonally distorted octahedral zinc complex that contains both a mono- and a bidentate benzene-1,2-diamine ligand (Qian *et al.*, 2007) and a distorted octahedral complex with *trans* monodentate benzene-1,2-diamine ligands (Ovalle-Marroquín *et al.*, 2002) have been reported.

### 5. Synthesis and crystallization

Compound (I) was prepared by mixing a solution of 100. mg (0.734 mmol) zinc chloride dissolved in approximately 5 mL ethanol with a solution of 238 mg (2.20 mmol) benzene-1,2-diamine dissolved in approximately 5 mL ethanol. The mixture became cloudy with a fine white precipitate. After the addition of 4 drops of 6 M HCl, the mixture was gently heated, filtered and allowed to slowly evaporate. After two days, 0.0273 g (0.117 mmol, 15% yield) of clear, colorless crystals were isolated, which were used for data collection. The diffraction pattern showed signs of degradation as the temperature was lowered to 200 K from 300 K and so data sets were collected at both temperatures.

Compound (II) was prepared by combining solutions of 100 mg (0.734 mmole) zinc chloride in a few mL of ethanol and 300 mg (2.20 mmol) 4,5-dimethylbenzene-1,2-diamine in a few mL of ethanol. After the addition of 4 drops of 6 M HCl, the mixture was gently heated and filtered. The filtrate was divided into three portions and each allowed to slowly evaporate. After several days, a small number of clear, colorless crystals in the shape of hexagonal plates were isolated, one of which was used for data collection.

**Table 7**  
Experimental details.

	(Ia)	(Ib)	(II)
Crystal data			
Chemical formula	[ZnCl <sub>2</sub> (C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> )]	[ZnCl <sub>2</sub> (C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> )]	[Zn(C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> ·2C <sub>8</sub> H <sub>12</sub> N <sub>2</sub>
<i>M<sub>r</sub></i>	244.41	244.41	717.08
Crystal system, space group	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>	Monoclinic, <i>P2<sub>1</sub>/c</i>
Temperature (K)	300	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.4039 (9), 7.5206 (7), 14.1667 (15)	8.4152 (12), 7.5141 (9), 14.199 (2)	18.529 (2), 12.6227 (16), 7.8691 (8)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 90, 90	90, 90, 90	90, 94.665 (4), 90
<i>V</i> (Å <sup>3</sup> )	895.37 (16)	897.8 (2)	1834.4 (4)
<i>Z</i>	4	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	3.27	3.27	0.86
Crystal size (mm)	0.60 × 0.30 × 0.20	0.60 × 0.30 × 0.20	0.60 × 0.40 × 0.10
Data collection			
Diffractometer	Bruker SMART X2S benchtop	Bruker SMART X2S benchtop	Bruker SMART X2S benchtop
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.39, 0.56	0.40, 0.56	0.66, 0.92
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	9435, 1129, 1026	4392, 1090, 992	25430, 3619, 2920
<i>R<sub>int</sub></i>	0.039	0.040	0.060
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.658	0.649	0.617
Refinement			
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.020, 0.051, 1.09	0.027, 0.074, 1.16	0.031, 0.079, 1.05
No. of reflections	1129	1090	3619
No. of parameters	72	72	245
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.26, -0.40	0.41, -0.58	0.31, -0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

## 6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 7. For compound (I), data sets were collected at 300 K (Ia) and 200 K (Ib). The diffraction pattern showed clear degradation at the lower temperature. Examination of the crystal subjected to the cold stream showed fractures that were not previously present. As seen in Table 7, the cell constant s.u.s., *R* values and *S* values are lower for the 300 K data set.

For both (I) and (II), all hydrogen atoms were located in difference Fourier maps. For (I), all hydrogen atoms bonded to the nitrogen atoms were refined freely, including isotropic displacement parameters. For (Ia), the hydrogen atoms bonded to the benzene carbon atoms were refined using a riding model with C–H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C), whereas these hydrogen atoms were refined with C–H = 0.95 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for (Ib).

For (II), the amine hydrogen atoms of the non-coordinating 4,5-dimethylbenzene-1,2-diamine were refined freely, including the isotropic displacement parameters. For the hydrogen atoms of the coordinating amines, the atomic coordinates were refined freely with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N). The hydrogen atoms of the water ligands were refined freely, including the isotropic displacement parameters. The methyl

hydrogen atoms were refined with C–H = 0.98 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C).

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## supporting information

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## Structural characterization of two benzene-1,2-diamine complexes of zinc chloride: a molecular compound and a co-crystal salt

Patricia L. Zick and David K. Geiger

### Computing details

For all compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *S SAINT* (Bruker, 2013); data reduction: *S SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### (Ia) (Benzene-1,2-diamine- $\kappa^2N,N'$ )dichloridozinc

#### Crystal data

[ZnCl<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)]

$M_r = 244.41$

Orthorhombic, *Pnma*

$a = 8.4039$  (9) Å

$b = 7.5206$  (7) Å

$c = 14.1667$  (15) Å

$V = 895.37$  (16) Å<sup>3</sup>

$Z = 4$

$F(000) = 488$

$D_x = 1.813$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6300 reflections

$\theta = 2.8$ – $29.2^\circ$

$\mu = 3.27$  mm<sup>-1</sup>

$T = 300$  K

Parallelepiped, colorless

$0.60 \times 0.30 \times 0.20$  mm

#### Data collection

Bruker SMART X2S benchtop  
diffractometer

Radiation source: sealed microfocus tube

Doubly curved silicon crystal monochromator

Detector resolution: 8.3330 pixels mm<sup>-1</sup>

/w scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2013)

$T_{\min} = 0.39$ ,  $T_{\max} = 0.56$

9435 measured reflections

1129 independent reflections

1026 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.9^\circ$ ,  $\theta_{\min} = 2.8^\circ$

$h = -11 \rightarrow 11$

$k = -9 \rightarrow 8$

$l = -18 \rightarrow 15$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.051$

$S = 1.09$

1129 reflections

72 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 0.2253P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.40$  e Å<sup>-3</sup>

*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.** Refined as a 2-component inversion twin.

*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	0.12910 (3)	0.75	0.38035 (2)	0.03301 (10)
N1	0.3667 (2)	0.75	0.34928 (13)	0.0359 (5)
H1	0.393 (2)	0.656 (3)	0.3182 (15)	0.050 (6)*
N2	0.1999 (2)	0.75	0.51849 (13)	0.0362 (5)
H2	0.162 (3)	0.660 (3)	0.5468 (16)	0.057 (6)*
C11	0.00181 (5)	0.50621 (6)	0.33277 (3)	0.04250 (13)
C1	0.4560 (3)	0.75	0.43712 (14)	0.0301 (4)
C2	0.3724 (2)	0.75	0.52146 (14)	0.0293 (4)
C3	0.4541 (3)	0.75	0.60645 (15)	0.0406 (5)
H3	0.3982	0.75	0.6631	0.049*
C4	0.6191 (3)	0.75	0.60699 (19)	0.0496 (7)
H4	0.6742	0.75	0.6639	0.059*
C5	0.7007 (3)	0.75	0.5231 (2)	0.0508 (7)
H5	0.8114	0.75	0.5236	0.061*
C6	0.6208 (3)	0.75	0.43830 (19)	0.0434 (6)
H6	0.6774	0.75	0.3819	0.052*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.03143 (15)	0.04349 (19)	0.02409 (14)	0	-0.00277 (9)	0
N1	0.0353 (10)	0.0523 (14)	0.0200 (8)	0	0.0028 (7)	0
N2	0.0357 (10)	0.0506 (14)	0.0223 (8)	0	0.0037 (7)	0
C11	0.0528 (3)	0.0391 (3)	0.0355 (2)	-0.00706 (18)	-0.00622 (16)	0.00356 (16)
C1	0.0339 (11)	0.0307 (12)	0.0258 (9)	0	0.0001 (8)	0
C2	0.0342 (11)	0.0308 (12)	0.0228 (9)	0	-0.0010 (7)	0
C3	0.0499 (14)	0.0474 (15)	0.0244 (10)	0	-0.0057 (9)	0
C4	0.0485 (15)	0.0559 (18)	0.0443 (14)	0	-0.0201 (11)	0
C5	0.0354 (13)	0.0582 (18)	0.0587 (15)	0	-0.0093 (11)	0
C6	0.0332 (12)	0.0541 (17)	0.0429 (13)	0	0.0041 (9)	0

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

Zn1—C11 <sup>i</sup>	2.2271 (5)	C5—C6	1.377 (4)
Zn1—C11	2.2271 (5)	C5—H5	0.93
Zn1—N1	2.0449 (19)	C4—C5	1.372 (4)
Zn1—N2	2.0454 (18)	C4—H4	0.93
N2—C2	1.451 (3)	C3—C4	1.387 (4)



N2—H2	0.85 (2)	C3—H3	0.93
N1—C1	1.453 (3)	C2—C3	1.386 (3)
N1—H1	0.86 (2)	C1—C2	1.386 (3)
C6—H6	0.93	C1—C6	1.385 (3)
C11—Zn1—C11 <sup>i</sup>	110.82 (2)	C4—C5—C6	120.8 (2)
N1—Zn1—N2	85.53 (8)	C6—C5—H5	119.6
N1—Zn1—C11	113.82 (3)	C4—C5—H5	119.6
N2—Zn1—C11	115.42 (3)	C5—C4—C3	119.7 (2)
N2—Zn1—C11 <sup>i</sup>	115.42 (3)	C5—C4—H4	120.2
N1—Zn1—C11 <sup>i</sup>	113.82 (3)	C3—C4—H4	120.2
Zn1—N2—H2	110.1 (15)	C2—C3—C4	120.0 (2)
C2—N2—H2	111.3 (15)	C4—C3—H3	120.0
C2—N2—Zn1	108.56 (13)	C2—C3—H3	120.0
Zn1—N1—H1	111.1 (14)	C3—C2—C1	119.8 (2)
C1—N1—H1	107.8 (14)	C3—C2—N2	121.4 (2)
C1—N1—Zn1	108.67 (13)	C1—C2—N2	118.81 (18)
C5—C6—C1	119.9 (2)	C6—C1—C2	119.8 (2)
C5—C6—H6	120.1	C6—C1—N1	121.79 (19)
C1—C6—H6	120.1	C2—C1—N1	118.43 (19)

Symmetry code: (i)  $x, -y+3/2, z$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ C11 <sup>ii</sup>	0.86 (2)	2.59 (2)	3.3618 (16)	150.7 (18)
N2—H2 $\cdots$ C11 <sup>iii</sup>	0.85 (2)	2.52 (2)	3.3204 (16)	157 (2)

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

### (II) *trans*-Diaquabis(4,5-dimethylbenzene-1,2-diamine- $\kappa^2N,N'$ )zinc chloride-4,5-dimethylbenzene-1,2-diamine (1/2)

#### Crystal data

$[\text{Zn}(\text{C}_8\text{H}_{12}\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 2\text{C}_8\text{H}_{12}\text{N}_2$

$M_r = 717.08$

Monoclinic,  $P2_1/c$

$a = 18.529 (2) \text{\AA}$

$b = 12.6227 (16) \text{\AA}$

$c = 7.8691 (8) \text{\AA}$

$\beta = 94.665 (4)^\circ$

$V = 1834.4 (4) \text{\AA}^3$

$Z = 2$

$F(000) = 760$

$D_x = 1.298 \text{ Mg m}^{-3}$

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

Cell parameters from 8719 reflections

$\theta = 2.7\text{--}25.8^\circ$

$\mu = 0.86 \text{ mm}^{-1}$

$T = 200 \text{ K}$

Plate, clear colourless

$0.60 \times 0.40 \times 0.10 \text{ mm}$

#### Data collection

Bruker SMART X2S benchtop  
diffractometer

Radiation source: sealed microfocus tube

Doubly curved silicon crystal monochromator

Detector resolution:  $8.3330 \text{ pixels mm}^{-1}$

/w scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2013)

$T_{\min} = 0.66, T_{\max} = 0.92$

25430 measured reflections

3619 independent reflections

2920 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$   
 $\theta_{\text{max}} = 26.0^\circ$ ,  $\theta_{\text{min}} = 2.7^\circ$   
 $h = -22 \rightarrow 22$

$k = -15 \rightarrow 15$   
 $l = -9 \rightarrow 9$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.079$   
 $S = 1.05$   
 3619 reflections  
 245 parameters  
 0 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 0.4174P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$

### 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.

### 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	0.5	0.5	0.5	0.02953 (11)
Cl1	0.45668 (3)	0.33892 (4)	1.02374 (6)	0.03564 (13)
O1	0.56720 (9)	0.42255 (13)	0.31090 (19)	0.0392 (4)
H1WA	0.6043 (14)	0.447 (2)	0.278 (3)	0.051 (8)*
H1WB	0.5410 (14)	0.403 (2)	0.231 (3)	0.058 (8)*
N1	0.40508 (8)	0.41964 (13)	0.4016 (2)	0.0274 (3)
H1A	0.4163 (11)	0.3837 (17)	0.317 (3)	0.033*
H1B	0.3870 (11)	0.3749 (17)	0.468 (3)	0.033*
N2	0.45593 (9)	0.61470 (14)	0.3192 (2)	0.0322 (4)
H2A	0.4637 (11)	0.6792 (18)	0.355 (3)	0.039*
H2B	0.4755 (12)	0.6043 (17)	0.233 (3)	0.039*
N3	0.67491 (11)	0.80052 (17)	0.8184 (3)	0.0422 (4)
H3A	0.6415 (14)	0.807 (2)	0.741 (3)	0.056 (8)*
H3B	0.6781 (12)	0.736 (2)	0.859 (3)	0.050 (7)*
N4	0.68407 (11)	0.98800 (18)	0.6276 (3)	0.0408 (4)
H4A	0.6917 (13)	1.035 (2)	0.560 (3)	0.058 (8)*
H4B	0.6509 (14)	0.947 (2)	0.579 (3)	0.053 (7)*
C1	0.35297 (10)	0.49852 (14)	0.3405 (2)	0.0261 (4)
C2	0.37896 (10)	0.59711 (15)	0.2950 (2)	0.0280 (4)
C3	0.33004 (11)	0.67499 (16)	0.2373 (2)	0.0356 (5)
H3	0.3479	0.7416	0.2031	0.043*
C4	0.25549 (11)	0.65820 (17)	0.2281 (2)	0.0385 (5)
C5	0.22942 (10)	0.56000 (18)	0.2798 (2)	0.0373 (5)
C6	0.27863 (10)	0.48108 (16)	0.3337 (2)	0.0325 (5)
H6	0.2611	0.414	0.3666	0.039*
C7	0.20454 (14)	0.7463 (2)	0.1635 (3)	0.0584 (7)
H7A	0.2328	0.8085	0.1351	0.088*

H7B	0.1726	0.7651	0.2522	0.088*
H7C	0.1753	0.7221	0.0615	0.088*
C8	0.14910 (12)	0.5376 (2)	0.2831 (3)	0.0575 (7)
H8A	0.1248	0.5496	0.1694	0.086*
H8B	0.1285	0.5849	0.3653	0.086*
H8C	0.1421	0.4638	0.3168	0.086*
C9	0.74336 (10)	0.84050 (16)	0.7842 (2)	0.0337 (4)
C10	0.74828 (10)	0.93442 (16)	0.6917 (2)	0.0330 (4)
C11	0.81603 (12)	0.97694 (17)	0.6739 (3)	0.0389 (5)
H11	0.8193	1.0404	0.61	0.047*
C12	0.87968 (11)	0.93093 (19)	0.7455 (3)	0.0437 (5)
C13	0.87500 (12)	0.83640 (19)	0.8363 (3)	0.0441 (5)
C14	0.80689 (12)	0.79322 (18)	0.8537 (2)	0.0403 (5)
H14	0.8036	0.7289	0.9154	0.048*
C15	0.95146 (14)	0.9844 (2)	0.7237 (4)	0.0706 (8)
H15A	0.9767	0.9977	0.836	0.106*
H15B	0.9429	1.0518	0.6636	0.106*
H15C	0.9812	0.9384	0.6575	0.106*
C16	0.94172 (14)	0.7809 (3)	0.9159 (3)	0.0710 (8)
H16A	0.9745	0.7651	0.8275	0.107*
H16B	0.9275	0.7147	0.9691	0.107*
H16C	0.9664	0.8268	1.0026	0.107*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.02417 (16)	0.03331 (19)	0.03039 (18)	−0.00446 (13)	−0.00213 (12)	−0.00003 (13)
Cl1	0.0358 (3)	0.0413 (3)	0.0299 (3)	−0.0041 (2)	0.00360 (19)	0.0004 (2)
O1	0.0308 (8)	0.0510 (10)	0.0362 (9)	−0.0069 (7)	0.0048 (7)	−0.0091 (7)
N1	0.0275 (8)	0.0270 (9)	0.0280 (9)	−0.0030 (7)	0.0028 (7)	−0.0012 (7)
N2	0.0310 (9)	0.0344 (9)	0.0318 (9)	−0.0076 (7)	0.0061 (7)	0.0018 (8)
N3	0.0411 (11)	0.0428 (12)	0.0436 (11)	−0.0114 (9)	0.0094 (9)	−0.0012 (9)
N4	0.0359 (10)	0.0443 (12)	0.0422 (11)	−0.0001 (9)	0.0027 (8)	0.0053 (10)
C1	0.0261 (9)	0.0311 (10)	0.0209 (9)	−0.0002 (8)	0.0004 (7)	−0.0021 (8)
C2	0.0287 (9)	0.0329 (10)	0.0225 (9)	−0.0024 (8)	0.0019 (7)	0.0002 (8)
C3	0.0435 (11)	0.0314 (11)	0.0318 (11)	0.0007 (9)	0.0024 (9)	0.0035 (8)
C4	0.0401 (11)	0.0471 (13)	0.0279 (10)	0.0131 (10)	0.0005 (8)	−0.0020 (9)
C5	0.0279 (10)	0.0544 (14)	0.0297 (10)	0.0019 (9)	0.0020 (8)	−0.0012 (9)
C6	0.0273 (10)	0.0400 (12)	0.0301 (10)	−0.0055 (8)	0.0024 (8)	0.0004 (8)
C7	0.0582 (15)	0.0603 (17)	0.0559 (15)	0.0239 (13)	−0.0010 (12)	0.0009 (12)
C8	0.0301 (12)	0.0844 (19)	0.0582 (15)	0.0066 (12)	0.0043 (11)	0.0051 (13)
C9	0.0359 (11)	0.0376 (12)	0.0288 (10)	−0.0068 (9)	0.0093 (8)	−0.0070 (9)
C10	0.0354 (11)	0.0364 (11)	0.0276 (10)	−0.0011 (9)	0.0060 (8)	−0.0047 (8)
C11	0.0405 (12)	0.0393 (12)	0.0379 (11)	−0.0076 (9)	0.0089 (9)	0.0030 (9)
C12	0.0342 (11)	0.0583 (15)	0.0394 (12)	−0.0083 (10)	0.0071 (9)	−0.0055 (11)
C13	0.0389 (12)	0.0572 (15)	0.0361 (11)	0.0042 (11)	0.0025 (9)	−0.0024 (10)
C14	0.0493 (13)	0.0380 (12)	0.0342 (11)	0.0031 (10)	0.0069 (9)	0.0025 (9)
C15	0.0383 (14)	0.100 (2)	0.0741 (19)	−0.0179 (14)	0.0070 (13)	0.0068 (16)

C16    0.0503 (15)    0.095 (2)    0.0656 (17)    0.0143 (15)    -0.0073 (13)    0.0084 (16)

*Geometric parameters (Å, °)*

Zn1—N1 <sup>i</sup>	2.1214 (15)	C4—C7	1.519 (3)
Zn1—N1	2.1214 (15)	C5—C6	1.393 (3)
Zn1—N2	2.1442 (17)	C5—C8	1.517 (3)
Zn1—N2 <sup>i</sup>	2.1442 (17)	C6—H6	0.95
Zn1—O1 <sup>i</sup>	2.2409 (15)	C7—H7A	0.98
Zn1—O1	2.2410 (15)	C7—H7B	0.98
O1—H1WA	0.81 (3)	C7—H7C	0.98
O1—H1WB	0.80 (3)	C8—H8A	0.98
N1—C1	1.442 (2)	C8—H8B	0.98
N1—H1A	0.84 (2)	C8—H8C	0.98
N1—H1B	0.85 (2)	C9—C14	1.391 (3)
N2—C2	1.441 (2)	C9—C10	1.398 (3)
N2—H2A	0.87 (2)	C10—C11	1.383 (3)
N2—H2B	0.81 (2)	C11—C12	1.392 (3)
N3—C9	1.411 (3)	C11—H11	0.95
N3—H3A	0.84 (3)	C12—C13	1.397 (3)
N3—H3B	0.87 (3)	C12—C15	1.514 (3)
N4—C10	1.425 (3)	C13—C14	1.392 (3)
N4—H4A	0.81 (3)	C13—C16	1.512 (3)
N4—H4B	0.87 (3)	C14—H14	0.95
C1—C6	1.392 (2)	C15—H15A	0.98
C1—C2	1.392 (3)	C15—H15B	0.98
C2—C3	1.388 (3)	C15—H15C	0.98
C3—C4	1.393 (3)	C16—H16A	0.98
C3—H3	0.95	C16—H16B	0.98
C4—C5	1.403 (3)	C16—H16C	0.98
N1 <sup>i</sup> —Zn1—N1	180.0	C6—C5—C4	119.21 (18)
N1 <sup>i</sup> —Zn1—N2	100.31 (6)	C6—C5—C8	118.7 (2)
N1—Zn1—N2	79.69 (6)	C4—C5—C8	122.1 (2)
N1 <sup>i</sup> —Zn1—N2 <sup>i</sup>	79.69 (6)	C1—C6—C5	121.32 (19)
N1—Zn1—N2 <sup>i</sup>	100.31 (6)	C1—C6—H6	119.3
N2—Zn1—N2 <sup>i</sup>	180.0	C5—C6—H6	119.3
N1 <sup>i</sup> —Zn1—O1 <sup>i</sup>	92.18 (7)	C4—C7—H7A	109.5
N1—Zn1—O1 <sup>i</sup>	87.82 (7)	C4—C7—H7B	109.5
N2—Zn1—O1 <sup>i</sup>	86.78 (7)	H7A—C7—H7B	109.5
N2 <sup>i</sup> —Zn1—O1 <sup>i</sup>	93.22 (7)	C4—C7—H7C	109.5
N1 <sup>i</sup> —Zn1—O1	87.82 (7)	H7A—C7—H7C	109.5
N1—Zn1—O1	92.18 (7)	H7B—C7—H7C	109.5
N2—Zn1—O1	93.22 (7)	C5—C8—H8A	109.5
N2 <sup>i</sup> —Zn1—O1	86.78 (7)	C5—C8—H8B	109.5
O1 <sup>i</sup> —Zn1—O1	180.00 (5)	H8A—C8—H8B	109.5
Zn1—O1—H1WA	124.6 (18)	C5—C8—H8C	109.5
Zn1—O1—H1WB	108.7 (18)	H8A—C8—H8C	109.5

H1WA—O1—H1WB	110 (2)	H8B—C8—H8C	109.5
C1—N1—Zn1	107.71 (12)	C14—C9—C10	118.65 (18)
C1—N1—H1A	108.0 (14)	C14—C9—N3	121.1 (2)
Zn1—N1—H1A	107.1 (14)	C10—C9—N3	120.01 (19)
C1—N1—H1B	111.9 (14)	C11—C10—C9	118.68 (19)
Zn1—N1—H1B	116.6 (13)	C11—C10—N4	121.26 (19)
H1A—N1—H1B	105 (2)	C9—C10—N4	119.93 (18)
C2—N2—Zn1	107.66 (11)	C10—C11—C12	122.9 (2)
C2—N2—H2A	108.9 (14)	C10—C11—H11	118.5
Zn1—N2—H2A	111.8 (14)	C12—C11—H11	118.5
C2—N2—H2B	111.9 (15)	C11—C12—C13	118.52 (19)
Zn1—N2—H2B	106.0 (16)	C11—C12—C15	119.4 (2)
H2A—N2—H2B	111 (2)	C13—C12—C15	122.0 (2)
C9—N3—H3A	116.8 (17)	C14—C13—C12	118.65 (19)
C9—N3—H3B	111.6 (16)	C14—C13—C16	119.7 (2)
H3A—N3—H3B	112 (2)	C12—C13—C16	121.7 (2)
C10—N4—H4A	113.0 (18)	C9—C14—C13	122.6 (2)
C10—N4—H4B	114.7 (17)	C9—C14—H14	118.7
H4A—N4—H4B	107 (2)	C13—C14—H14	118.7
C6—C1—C2	119.58 (17)	C12—C15—H15A	109.5
C6—C1—N1	122.50 (17)	C12—C15—H15B	109.5
C2—C1—N1	117.84 (16)	H15A—C15—H15B	109.5
C3—C2—C1	119.14 (17)	C12—C15—H15C	109.5
C3—C2—N2	123.19 (18)	H15A—C15—H15C	109.5
C1—C2—N2	117.59 (16)	H15B—C15—H15C	109.5
C2—C3—C4	121.84 (19)	C13—C16—H16A	109.5
C2—C3—H3	119.1	C13—C16—H16B	109.5
C4—C3—H3	119.1	H16A—C16—H16B	109.5
C3—C4—C5	118.86 (18)	C13—C16—H16C	109.5
C3—C4—C7	119.5 (2)	H16A—C16—H16C	109.5
C5—C4—C7	121.6 (2)	H16B—C16—H16C	109.5
Zn1—N1—C1—C6	-152.85 (15)	C4—C5—C6—C1	1.3 (3)
Zn1—N1—C1—C2	24.00 (19)	C8—C5—C6—C1	-177.21 (19)
C6—C1—C2—C3	-2.4 (3)	C14—C9—C10—C11	-0.4 (3)
N1—C1—C2—C3	-179.38 (16)	N3—C9—C10—C11	173.98 (18)
C6—C1—C2—N2	174.28 (17)	C14—C9—C10—N4	-176.29 (18)
N1—C1—C2—N2	-2.7 (2)	N3—C9—C10—N4	-1.9 (3)
Zn1—N2—C2—C3	156.68 (15)	C9—C10—C11—C12	-0.7 (3)
Zn1—N2—C2—C1	-19.9 (2)	N4—C10—C11—C12	175.16 (19)
C1—C2—C3—C4	1.8 (3)	C10—C11—C12—C13	1.4 (3)
N2—C2—C3—C4	-174.74 (17)	C10—C11—C12—C15	-178.3 (2)
C2—C3—C4—C5	0.4 (3)	C11—C12—C13—C14	-1.1 (3)
C2—C3—C4—C7	-179.85 (18)	C15—C12—C13—C14	178.7 (2)
C3—C4—C5—C6	-1.9 (3)	C11—C12—C13—C16	179.2 (2)
C7—C4—C5—C6	178.34 (19)	C15—C12—C13—C16	-1.0 (3)
C3—C4—C5—C8	176.51 (19)	C10—C9—C14—C13	0.7 (3)
C7—C4—C5—C8	-3.2 (3)	N3—C9—C14—C13	-173.60 (19)

C2—C1—C6—C5	0.9 (3)	C12—C13—C14—C9	0.0 (3)
N1—C1—C6—C5	177.72 (17)	C16—C13—C14—C9	179.7 (2)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1WA $\cdots$ N4 <sup>ii</sup>	0.81 (3)	2.13 (3)	2.924 (3)	164 (2)
O1—H1WB $\cdots$ C11 <sup>iii</sup>	0.80 (3)	2.31 (3)	3.1083 (17)	173 (2)
N1—H1A $\cdots$ C11 <sup>iii</sup>	0.84 (2)	2.55 (2)	3.3551 (18)	160.3 (18)
N1—H1B $\cdots$ N3 <sup>iv</sup>	0.85 (2)	2.31 (2)	3.137 (3)	162.6 (18)
N2—H2A $\cdots$ C11 <sup>v</sup>	0.87 (2)	2.63 (2)	3.4401 (19)	155.3 (18)
N2—H2B $\cdots$ C11 <sup>i</sup>	0.81 (2)	2.57 (2)	3.3105 (18)	154 (2)
N3—H3A $\cdots$ C11 <sup>v</sup>	0.84 (3)	2.68 (3)	3.516 (2)	174 (2)
N3—H3B $\cdots$ C11 <sup>vi</sup>	0.87 (3)	2.89 (2)	3.3284 (19)	112.9 (18)
N4—H4B $\cdots$ C11 <sup>v</sup>	0.87 (3)	2.50 (3)	3.355 (2)	171 (2)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+3/2, z-1/2$ ; (iii)  $x, y, z-1$ ; (iv)  $-x+1, y-1/2, -z+3/2$ ; (v)  $-x+1, y+1/2, -z+3/2$ ; (vi)  $-x+1, -y+1, -z+2$ .

### (Ib) (Benzene-1,2-diamine- $\kappa^2N,N'$ )dichloridozinc

#### Crystal data

$[\text{ZnCl}_2(\text{C}_6\text{H}_8\text{N}_2)]$

$M_r = 244.41$

Orthorhombic,  $Pnma$

$a = 8.4152$  (12)  $\text{\AA}$

$b = 7.5141$  (9)  $\text{\AA}$

$c = 14.199$  (2)  $\text{\AA}$

$V = 897.8$  (2)  $\text{\AA}^3$

$Z = 4$

$F(000) = 488$

$D_x = 1.808$   $\text{Mg m}^{-3}$

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

Cell parameters from 2561 reflections

$\theta = 2.8\text{--}29.2^\circ$

$\mu = 3.27$   $\text{mm}^{-1}$

$T = 200$  K

Prism, clear colourless

$0.60 \times 0.30 \times 0.20$  mm

#### Data collection

Bruker SMART X2S benchtop  
diffractometer

Radiation source: XOS X-beam microfocus  
source

Doubly curved silicon crystal monochromator

Detector resolution: 8.3330 pixels  $\text{mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2013)

$T_{\min} = 0.40, T_{\max} = 0.56$

4392 measured reflections

1090 independent reflections

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

$R_{\text{int}} = 0.040$

$\theta_{\max} = 27.5^\circ, \theta_{\min} = 2.8^\circ$

$h = -10 \rightarrow 5$

$k = -8 \rightarrow 9$

$l = -15 \rightarrow 18$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.074$

$S = 1.16$

1090 reflections

72 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.41$   $\text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.58$   $\text{e \AA}^{-3}$

*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.** Refined as a 2-component inversion twin.

*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	0.12938 (3)	0.75	0.38034 (2)	0.03201 (15)
N1	0.3669 (2)	0.75	0.3494 (2)	0.0343 (6)
H1	0.388 (2)	0.661 (3)	0.318 (2)	0.040 (7)*
N2	0.2002 (3)	0.75	0.51812 (18)	0.0354 (6)
H2	0.165 (3)	0.666 (3)	0.550 (2)	0.047 (7)*
Cl1	0.00184 (5)	0.50585 (6)	0.33279 (4)	0.04089 (18)
C1	0.4559 (3)	0.75	0.4370 (2)	0.0294 (6)
C2	0.3728 (3)	0.75	0.5215 (2)	0.0284 (6)
C3	0.4543 (4)	0.75	0.6066 (2)	0.0402 (7)
H3	0.3973	0.75	0.6644	0.048*
C4	0.6198 (4)	0.75	0.6068 (3)	0.0482 (9)
H4	0.6761	0.75	0.6648	0.058*
C5	0.7015 (4)	0.75	0.5231 (3)	0.0493 (8)
H5	0.8144	0.75	0.5237	0.059*
C6	0.6220 (3)	0.75	0.4382 (3)	0.0423 (8)
H6	0.6798	0.75	0.3807	0.051*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0301 (2)	0.0408 (3)	0.0251 (2)	0	-0.00244 (10)	0
N1	0.0345 (12)	0.0468 (18)	0.0216 (12)	0	0.0024 (8)	0
N2	0.0346 (12)	0.0469 (17)	0.0246 (12)	0	0.0041 (9)	0
Cl1	0.0502 (3)	0.0367 (3)	0.0358 (3)	-0.0066 (2)	-0.0058 (2)	0.0032 (2)
C1	0.0341 (12)	0.0282 (14)	0.0259 (13)	0	-0.0001 (10)	0
C2	0.0309 (13)	0.0289 (14)	0.0253 (14)	0	-0.0005 (9)	0
C3	0.0498 (16)	0.0423 (17)	0.0283 (15)	0	-0.0035 (12)	0
C4	0.0487 (18)	0.051 (2)	0.045 (2)	0	-0.0201 (14)	0
C5	0.0331 (14)	0.053 (2)	0.061 (2)	0	-0.0120 (14)	0
C6	0.0331 (14)	0.051 (2)	0.0425 (19)	0	0.0048 (11)	0

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

Zn1—Cl1	2.2301 (5)	C5—C6	1.379 (5)
Zn1—Cl1 <sup>i</sup>	2.2301 (5)	C5—H5	0.95
Zn1—N1	2.047 (2)	C4—C5	1.373 (5)
Zn1—N2	2.045 (3)	C4—H4	0.95
N2—C2	1.453 (3)	C3—C4	1.393 (4)

N2—H2	0.83 (3)	C3—H3	0.95
N1—C1	1.452 (4)	C2—C3	1.389 (4)
N1—H1	0.83 (3)	C1—C2	1.388 (4)
C6—H6	0.95	C1—C6	1.398 (3)
C11—Zn1—C11 <sup>i</sup>	110.70 (3)	C4—C5—C6	120.9 (3)
N1—Zn1—N2	85.45 (10)	C6—C5—H5	119.5
N1—Zn1—C11	113.89 (4)	C4—C5—H5	119.5
N2—Zn1—C11 <sup>i</sup>	115.46 (3)	C5—C4—C3	119.9 (3)
N2—Zn1—C11	115.46 (3)	C5—C4—H4	120.0
N1—Zn1—C11 <sup>i</sup>	113.89 (4)	C3—C4—H4	120.0
Zn1—N2—H2	114.1 (19)	C2—C3—C4	119.7 (3)
C2—N2—H2	110.0 (17)	C4—C3—H3	120.2
C2—N2—Zn1	108.84 (19)	C2—C3—H3	120.2
Zn1—N1—H1	109.0 (14)	C1—C2—C3	120.2 (2)
C1—N1—H1	111.0 (18)	C3—C2—N2	121.5 (3)
C1—N1—Zn1	108.62 (18)	C1—C2—N2	118.4 (2)
C5—C6—C1	119.7 (3)	C2—C1—C6	119.6 (3)
C5—C6—H6	120.2	C6—C1—N1	121.7 (3)
C1—C6—H6	120.2	C2—C1—N1	118.7 (2)
Zn1—N1—C1—C2	0	C1—C2—C3—C4	0.0000 (10)
Zn1—N1—C1—C6	180.0	N2—C2—C3—C4	180.0000 (10)
C6—C1—C2—C3	0.0000 (10)	C2—C3—C4—C5	0.0000 (10)
N1—C1—C2—C3	180.0000 (10)	C3—C4—C5—C6	0.0000 (10)
C6—C1—C2—N2	180.0	C4—C5—C6—C1	0.0000 (10)
N1—C1—C2—N2	0.0000 (10)	C2—C1—C6—C5	0.0000 (10)
Zn1—N2—C2—C1	0.0000 (10)	N1—C1—C6—C5	180.0000 (10)
Zn1—N2—C2—C3	180.0000 (10)		

Symmetry code: (i)  $x, -y+3/2, z$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ C11 <sup>ii</sup>	0.83 (3)	2.61 (3)	3.368 (2)	152 (2)
N2—H2 $\cdots$ C11 <sup>iii</sup>	0.83 (3)	2.53 (3)	3.327 (2)	160 (2)

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