

# [2-(2,2'-Bipyridin-6-yl- $\kappa^2N^1,N^{1'}$ )benzo[*b*][1,5]-naphthyridine- $\kappa N^1$ ]dichloridozinc

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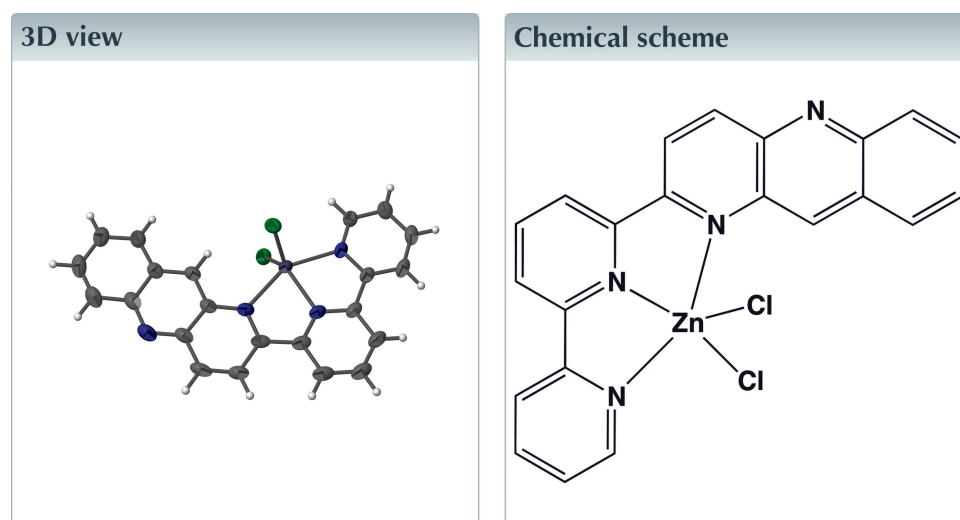
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Keywords: crystal structure; zinc(II) complex; NAD<sup>+</sup>/NADH-analogous ligand.

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Structural data: full structural data are available from iucrdata.iucr.org

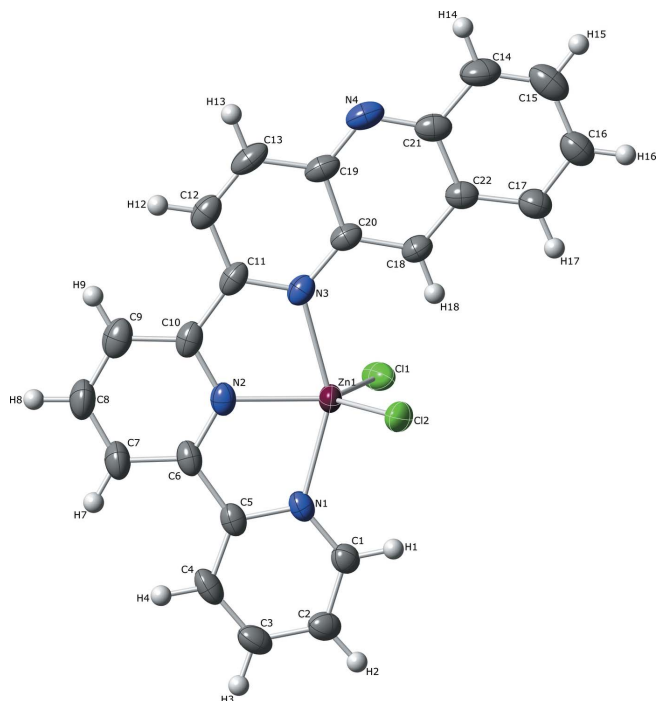
The coordination environment of the zinc(II) ion in the title complex, [ZnCl<sub>2</sub>(C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>)], is distorted trigonal-bipyramidal comprised by three N atoms from the 2-([2,2'-bipyridin]-6-yl)benzo[*b*][1,5]naphthyridine ligand and two Cl<sup>−</sup> ions. In the crystal, neighbouring molecules are connected by  $\pi$ – $\pi$  stacking interactions along the *a*-axis direction.



## Structure description

In order to gain valuable insights into the nature of the nicotinamide adenine dinucleotide (NAD) function and to develop photorenewable hydride reagents utilizing the NAD<sup>+</sup>/NADH redox function in NAD, we have so far investigated transition-metal complexes having NAD<sup>+</sup>/NADH-analogous ligands (Fukushima *et al.*, 2010; Ohtsu & Tanaka, 2012*a,b*; Ohtsu *et al.*, 2015, 2016). In this paper, a new zinc complex having a new NAD<sup>+</sup>/NADH-analogous ligand bbn (bbn = 2-([2,2'-bipyridin]-6-yl)benzo[*b*][1,5]-naphthyridine) has been synthesized and structurally characterized.

The molecular structure of the title complex, [Zn(bbn)Cl<sub>2</sub>], is shown in Fig. 1. The zinc(II) ion is surrounded by three N atoms from the bbn ligand and two Cl<sup>−</sup> ions. The bond lengths from the zinc to each of donor N atoms and chloride are Zn1–N1 = 2.191 (2), Zn1–N2 = 2.085 (2), Zn1–N3 = 2.230 (2), Zn1–Cl1 = 2.2732 (7) and Zn1–Cl2 = 2.2504 (7) Å. A range of five-coordinate geometries varying from trigonal-bipyramidal to square-pyramidal can be indicated by the  $\tau$  parameter ranging from  $\tau = 1$  for an ideal trigonal-bipyramidal geometry to  $\tau = 0$  for an ideal square-pyramidal geometry (Addison *et al.*, 1984). The  $\tau$  value for the zinc(II) ion in the title complex is obtained as  $\tau = 0.44$  by using the equation  $\tau = (\beta - \alpha)/60$  (Addison *et al.*, 1984), where  $\alpha = \text{N2–Zn1–Cl2}$  [123.76 (6)°],  $\beta = \text{N1–Zn1–N3}$  [150.24 (8)°]. In spite of the  $\tau$  value of 0.44, the coordination environment of the zinc(II) ion in [Zn(bbn)Cl<sub>2</sub>] can be better described as distorted trigonal-bipyramidal.



**Figure 1**  
The molecular structure of the title complex, with displacement ellipsoids at the 50% probability level.

This title complex presents intermolecular  $\pi$ - $\pi$  stacking interactions along the  $a$ -axis direction as shown in Fig. 2. The distances between the centroids of rings  $A$  (C14–17/C21/C22) and  $B$  (N1/C1–5)<sup>i</sup> [symmetry code: (i)  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ], and between the centroids of the rings  $C$  (N3/C11–13/C19/C20) and  $D$  (N1/C1–5)<sup>ii</sup> [symmetry code: (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ] are 3.5513 (3) and 3.5237 (3) Å, respectively.

### Synthesis and crystallization

The bbn ligand was prepared in the same manner as that for the synthesis of pbn (Koizumi & Tanaka, 2005) using 6-acetyl-2,2'-bipyridine (Vlugt *et al.*, 2008) instead of 2-acetyl-pyridine. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 9.13 (*d*, 1H), 9.10 (*s*, 1H), 8.79 (*dd*, 1H), 8.75–8.65 (*m*, 3H), 8.57 (*dd*, 1H), 8.29 (*dd*, 1H), 8.14 (*dt*, 1H), 8.07 (*t*, 1H), 7.96–7.82 (*m*, 2H), 7.63 (*ddd*, 1H), 7.38 (*ddd*, 1H).

To an acetonitrile solution (4 ml) of ZnCl<sub>2</sub> (20.4 mg, 0.15 mmol) was added dropwise bbn (50.0 mg, 0.15 mmol) in dichloromethane (4 ml). The resulting yellow precipitate was filtered and dissolved in hot methanol for recrystallization. After the solution was left to stand for a few weeks at room temperature, yellow crystals of the title complex [Zn(bbn)Cl<sub>2</sub>] were obtained (yield; 18.2 mg, 25.6%). Elemental analysis, found: C 55.82, H 2.99, N 11.71%; calculated for C<sub>22</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>4</sub>Zn: C 56.14, H 3.00, N 11.90%.

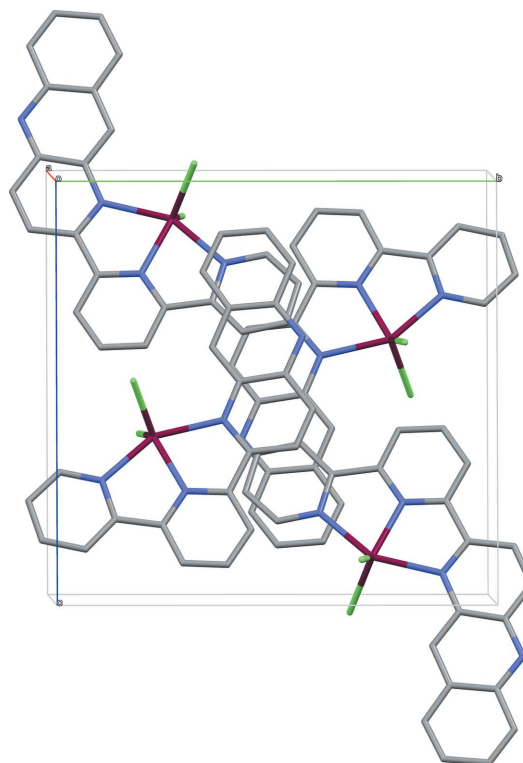
### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[ZnCl <sub>2</sub> (C <sub>22</sub> H <sub>14</sub> N <sub>4</sub> )]
<i>M<sub>r</sub></i>	470.67
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.8040 (2), 13.6433 (3), 13.2159 (3)
$\beta$ (°)	97.8812 (7)
<i>V</i> (Å <sup>3</sup> )	1929.65 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.57
Crystal size (mm)	0.08 × 0.08 × 0.07
Data collection	
Diffractometer	Rigaku R-Axis RAPID
Absorption correction	Multi-scan ( <i>ABSCOR</i> ; Higashi, 1995)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.718, 0.896
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	18736, 4400, 4050
<i>R<sub>int</sub></i>	0.026
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.648
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> [ <i>F</i> <sup>2</sup> ], <i>S</i>	0.038, 0.097, 1.12
No. of reflections	4400
No. of parameters	262
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.95, -0.35

Computer programs: *RAPID-AUTO* (Rigaku, 2001), *SIR2011* (Burla *et al.*, 2012), *SHELXL2016* (Sheldrick, 2015), *CrystalStructure* (Rigaku, 2016), *Mercury* (Macrae *et al.*, 2008), *CrystalMaker* (Palmer, 2007) and *pubCIF* (Westrip, 2010).



**Figure 2**  
The crystal packing of the title complex viewed along the  $a$  axis. H atoms have been omitted for clarity.

## Acknowledgements

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## References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Mallamo, M., Mazzone, A., Polidori, G. & Spagna, R. (2012). *J. Appl. Cryst.* **45**, 357–361.
- Fukushima, T., Wada, T., Ohtsu, H. & Tanaka, K. (2010). *Dalton Trans.* **39**, 11526–11534.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Koizumi, T.-a. & Tanaka, K. (2005). *Angew. Chem. Int. Ed.* **44**, 5891–5894.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Ohtsu, H., Fujii, S., Tsuge, K. & Tanaka, K. (2016). *Dalton Trans.* **45**, 16130–16133.
- Ohtsu, H. & Tanaka, K. (2012a). *Chem. Commun.* **48**, 1796–1798.
- Ohtsu, H. & Tanaka, K. (2012b). *Angew. Chem. Int. Ed.* **51**, 9792–9795.
- Ohtsu, H., Tsuge, K. & Tanaka, K. (2015). *J. Photochem. Photobiol. Chem.* **313**, 163–167.
- Palmer, D. (2007). *CrystalMaker*. Crystal Maker, Bicester, England.
- Rigaku (2001). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2016). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
- Vlugt, J. I. van der, Demeshko, S., Dechert, S. & Meyer, F. (2008). *Inorg. Chem.* **47**, 1576–1585.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## full crystallographic data

*IUCrData* (2016). **1**, x161779 [<https://doi.org/10.1107/S241431461601779X>]

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**[2-(2,2'-Bipyridin-6-yl- $\kappa^2N^1,N^1'$ )benzo[*b*][1,5]naphthyridine- $\kappa N^1$ ]dichloridozinc**

*Crystal data*

[ZnCl<sub>2</sub>(C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>)]

*M<sub>r</sub>* = 470.67

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 10.8040 (2) Å

*b* = 13.6433 (3) Å

*c* = 13.2159 (3) Å

$\beta$  = 97.8812 (7)°

*V* = 1929.65 (7) Å<sup>3</sup>

*Z* = 4

*F*(000) = 952.00

*D<sub>x</sub>* = 1.620 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71075 Å

Cell parameters from 16370 reflections

$\theta$  = 3.0–27.4°

$\mu$  = 1.57 mm<sup>-1</sup>

*T* = 173 K

Block, yellow

0.08 × 0.08 × 0.07 mm

*Data collection*

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

*T<sub>min</sub>* = 0.718, *T<sub>max</sub>* = 0.896

18736 measured reflections

4400 independent reflections

4050 reflections with  $F^2 > 2.0\sigma(F^2)$

*R<sub>int</sub>* = 0.026

$\theta_{\max}$  = 27.4°,  $\theta_{\min}$  = 3.0°

*h* = -13→14

*k* = -17→17

*l* = -16→17

*Refinement*

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.097$

*S* = 1.12

4400 reflections

262 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 2.004P]$

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

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

$\Delta\rho_{\max} = 0.95 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$

*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.** Refinement was performed using all reflections. The weighted R-factor (*wR*) and goodness of fit (*S*) are based on  $F^2$ . R-factor (*gt*) are based on *F*. The threshold expression of  $F^2 > 2.0 \sigma(F^2)$  is used only for calculating R-factor (*gt*).

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	0.14600 (3)	0.22246 (2)	0.60516 (2)	0.02931 (10)
CL1	0.35323 (6)	0.19462 (5)	0.60386 (5)	0.04174 (16)
CL2	0.00807 (7)	0.17449 (5)	0.47109 (5)	0.03958 (16)
N1	0.10596 (19)	0.10447 (16)	0.70834 (14)	0.0311 (4)
N2	0.09581 (19)	0.29423 (16)	0.73276 (16)	0.0323 (4)
N3	0.15042 (19)	0.38149 (15)	0.56697 (16)	0.0317 (4)
N4	0.2032 (2)	0.56306 (16)	0.3716 (2)	0.0424 (5)
C1	0.1099 (2)	0.00880 (19)	0.68850 (19)	0.0342 (5)
H1	0.132729	-0.011245	0.624729	0.041*
C2	0.0824 (3)	-0.0629 (2)	0.7564 (2)	0.0387 (6)
H2	0.087495	-0.130494	0.740161	0.046*
C3	0.0476 (3)	-0.0333 (2)	0.8480 (2)	0.0423 (6)
H3	0.028589	-0.080493	0.896416	0.051*
C4	0.0406 (3)	0.0652 (2)	0.86885 (19)	0.0406 (6)
H4	0.014766	0.086496	0.931137	0.049*
C5	0.0715 (2)	0.1336 (2)	0.79818 (18)	0.0324 (5)
C6	0.0691 (2)	0.2413 (2)	0.81226 (19)	0.0351 (5)
C7	0.0414 (3)	0.2863 (2)	0.9013 (2)	0.0470 (7)
H7	0.021399	0.248685	0.957327	0.056*
C8	0.0440 (3)	0.3871 (3)	0.9053 (2)	0.0526 (8)
H8	0.026562	0.419459	0.965325	0.063*
C9	0.0717 (3)	0.4421 (2)	0.8232 (2)	0.0454 (7)
H9	0.073696	0.511692	0.826419	0.055*
C10	0.0967 (2)	0.3928 (2)	0.7355 (2)	0.0358 (5)
C11	0.1253 (2)	0.44115 (18)	0.6410 (2)	0.0341 (5)
C12	0.1246 (2)	0.54527 (19)	0.6295 (2)	0.0386 (6)
H12	0.105882	0.586341	0.683423	0.046*
C13	0.1508 (2)	0.58476 (19)	0.5410 (2)	0.0418 (6)
H13	0.150643	0.653960	0.533003	0.050*
C14	0.2521 (3)	0.5421 (2)	0.2008 (3)	0.0526 (8)
H14	0.254409	0.611196	0.192511	0.063*
C15	0.2746 (3)	0.4838 (3)	0.1234 (2)	0.0535 (8)
H15	0.294094	0.512598	0.062067	0.064*
C16	0.2700 (3)	0.3804 (3)	0.1316 (2)	0.0472 (7)
H16	0.285278	0.340550	0.075634	0.057*
C17	0.2437 (3)	0.3380 (2)	0.2195 (2)	0.0427 (6)
H17	0.240144	0.268636	0.224379	0.051*
C18	0.1986 (2)	0.35777 (18)	0.3966 (2)	0.0350 (5)
H18	0.197990	0.288697	0.405575	0.042*
C19	0.1787 (2)	0.52359 (18)	0.4595 (2)	0.0353 (5)
C20	0.1766 (2)	0.41966 (17)	0.47647 (19)	0.0316 (5)
C21	0.2247 (2)	0.5025 (2)	0.2952 (2)	0.0386 (6)
C22	0.2214 (2)	0.39714 (19)	0.3045 (2)	0.0348 (5)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
ZN1	0.03447 (16)	0.02843 (15)	0.02587 (15)	0.00193 (10)	0.00711 (11)	-0.00438 (10)
CL1	0.0385 (3)	0.0367 (3)	0.0536 (4)	0.0085 (3)	0.0192 (3)	0.0075 (3)
CL2	0.0525 (4)	0.0360 (3)	0.0293 (3)	-0.0078 (3)	0.0021 (3)	-0.0062 (2)
N1	0.0297 (10)	0.0408 (11)	0.0230 (9)	-0.0008 (8)	0.0043 (7)	-0.0005 (8)
N2	0.0292 (10)	0.0378 (11)	0.0296 (10)	0.0037 (8)	0.0033 (8)	-0.0088 (8)
N3	0.0298 (10)	0.0284 (10)	0.0359 (11)	0.0027 (8)	0.0002 (8)	-0.0058 (8)
N4	0.0390 (12)	0.0280 (11)	0.0578 (15)	-0.0030 (9)	-0.0022 (10)	0.0031 (10)
C1	0.0352 (12)	0.0379 (13)	0.0290 (12)	-0.0033 (10)	0.0026 (9)	-0.0006 (10)
C2	0.0384 (14)	0.0403 (14)	0.0357 (14)	-0.0071 (11)	-0.0011 (10)	0.0032 (11)
C3	0.0415 (14)	0.0531 (17)	0.0317 (13)	-0.0083 (12)	0.0026 (10)	0.0098 (11)
C4	0.0361 (13)	0.0625 (18)	0.0241 (12)	-0.0003 (12)	0.0069 (10)	0.0024 (11)
C5	0.0267 (11)	0.0448 (14)	0.0257 (11)	0.0016 (10)	0.0035 (9)	-0.0021 (10)
C6	0.0287 (12)	0.0499 (15)	0.0269 (12)	0.0038 (11)	0.0048 (9)	-0.0052 (10)
C7	0.0525 (17)	0.0563 (18)	0.0343 (14)	0.0067 (14)	0.0137 (12)	-0.0090 (12)
C8	0.0576 (18)	0.060 (2)	0.0421 (16)	0.0051 (15)	0.0148 (13)	-0.0171 (14)
C9	0.0438 (15)	0.0411 (15)	0.0510 (17)	0.0050 (12)	0.0050 (12)	-0.0175 (12)
C10	0.0264 (11)	0.0411 (14)	0.0387 (13)	0.0036 (10)	0.0000 (9)	-0.0122 (11)
C11	0.0256 (11)	0.0310 (12)	0.0436 (14)	0.0036 (9)	-0.0022 (10)	-0.0113 (10)
C12	0.0314 (12)	0.0314 (13)	0.0514 (16)	0.0028 (10)	0.0002 (11)	-0.0121 (11)
C13	0.0339 (13)	0.0226 (11)	0.0650 (18)	0.0028 (10)	-0.0066 (12)	-0.0071 (11)
C14	0.0563 (18)	0.0423 (16)	0.0577 (19)	-0.0096 (14)	0.0032 (14)	0.0151 (14)
C15	0.0502 (17)	0.064 (2)	0.0461 (17)	-0.0095 (15)	0.0075 (13)	0.0184 (15)
C16	0.0427 (15)	0.0589 (18)	0.0408 (15)	-0.0016 (13)	0.0088 (12)	0.0064 (13)
C17	0.0460 (15)	0.0411 (15)	0.0418 (15)	0.0001 (12)	0.0088 (12)	0.0061 (11)
C18	0.0372 (13)	0.0260 (11)	0.0413 (14)	0.0007 (10)	0.0043 (10)	-0.0002 (10)
C19	0.0273 (11)	0.0254 (11)	0.0508 (15)	-0.0013 (9)	-0.0036 (10)	0.0013 (10)
C20	0.0254 (11)	0.0263 (11)	0.0414 (13)	0.0010 (9)	-0.0017 (9)	0.0002 (9)
C21	0.0297 (12)	0.0361 (13)	0.0479 (15)	-0.0039 (10)	-0.0020 (10)	0.0076 (11)
C22	0.0297 (12)	0.0329 (13)	0.0411 (14)	0.0000 (10)	0.0018 (10)	0.0053 (10)

*Geometric parameters (Å, °)*

ZN1—N2	2.085 (2)	C8—C9	1.385 (5)
ZN1—N1	2.191 (2)	C8—H8	0.9500
ZN1—N3	2.230 (2)	C9—C10	1.398 (4)
ZN1—CL2	2.2504 (7)	C9—H9	0.9500
ZN1—CL1	2.2732 (7)	C10—C11	1.482 (4)
N1—C1	1.333 (3)	C11—C12	1.429 (4)
N1—C5	1.352 (3)	C12—C13	1.352 (4)
N2—C6	1.339 (3)	C12—H12	0.9500
N2—C10	1.345 (3)	C13—C19	1.427 (4)
N3—C11	1.329 (3)	C13—H13	0.9500
N3—C20	1.369 (3)	C14—C15	1.344 (5)
N4—C19	1.340 (4)	C14—C21	1.427 (4)
N4—C21	1.349 (4)	C14—H14	0.9500

C1—C2	1.387 (4)	C15—C16	1.417 (5)
C1—H1	0.9500	C15—H15	0.9500
C2—C3	1.377 (4)	C16—C17	1.363 (4)
C2—H2	0.9500	C16—H16	0.9500
C3—C4	1.377 (4)	C17—C22	1.430 (4)
C3—H3	0.9500	C17—H17	0.9500
C4—C5	1.393 (4)	C18—C22	1.383 (4)
C4—H4	0.9500	C18—C20	1.397 (4)
C5—C6	1.481 (4)	C18—H18	0.9500
C6—C7	1.396 (4)	C19—C20	1.436 (3)
C7—C8	1.375 (5)	C21—C22	1.444 (4)
C7—H7	0.9500		
N2—ZN1—N1	75.30 (8)	C9—C8—H8	119.4
N2—ZN1—N3	75.05 (8)	C8—C9—C10	118.3 (3)
N1—ZN1—N3	150.24 (8)	C8—C9—H9	120.8
N2—ZN1—CL2	123.76 (6)	C10—C9—H9	120.8
N1—ZN1—CL2	96.34 (6)	N2—C10—C9	120.1 (3)
N3—ZN1—CL2	97.88 (5)	N2—C10—C11	115.1 (2)
N2—ZN1—CL1	116.76 (6)	C9—C10—C11	124.8 (3)
N1—ZN1—CL1	99.25 (6)	N3—C11—C12	122.0 (3)
N3—ZN1—CL1	96.27 (6)	N3—C11—C10	115.8 (2)
CL2—ZN1—CL1	119.48 (3)	C12—C11—C10	122.2 (2)
C1—N1—C5	118.7 (2)	C13—C12—C11	119.3 (3)
C1—N1—ZN1	125.63 (16)	C13—C12—H12	120.4
C5—N1—ZN1	115.62 (17)	C11—C12—H12	120.4
C6—N2—C10	121.3 (2)	C12—C13—C19	120.7 (2)
C6—N2—ZN1	119.28 (17)	C12—C13—H13	119.6
C10—N2—ZN1	119.31 (18)	C19—C13—H13	119.6
C11—N3—C20	119.8 (2)	C15—C14—C21	121.5 (3)
C11—N3—ZN1	114.62 (18)	C15—C14—H14	119.2
C20—N3—ZN1	125.54 (16)	C21—C14—H14	119.2
C19—N4—C21	118.5 (2)	C14—C15—C16	121.3 (3)
N1—C1—C2	123.2 (2)	C14—C15—H15	119.4
N1—C1—H1	118.4	C16—C15—H15	119.4
C2—C1—H1	118.4	C17—C16—C15	120.1 (3)
C3—C2—C1	118.1 (3)	C17—C16—H16	120.0
C3—C2—H2	121.0	C15—C16—H16	120.0
C1—C2—H2	121.0	C16—C17—C22	120.5 (3)
C4—C3—C2	119.5 (3)	C16—C17—H17	119.7
C4—C3—H3	120.3	C22—C17—H17	119.7
C2—C3—H3	120.3	C22—C18—C20	120.0 (2)
C3—C4—C5	119.7 (2)	C22—C18—H18	120.0
C3—C4—H4	120.2	C20—C18—H18	120.0
C5—C4—H4	120.2	N4—C19—C13	120.5 (2)
N1—C5—C4	120.8 (2)	N4—C19—C20	122.8 (2)
N1—C5—C6	114.4 (2)	C13—C19—C20	116.7 (2)
C4—C5—C6	124.8 (2)	N3—C20—C18	120.5 (2)

N2—C6—C7	121.2 (3)	N3—C20—C19	121.4 (2)
N2—C6—C5	115.3 (2)	C18—C20—C19	118.1 (2)
C7—C6—C5	123.5 (3)	N4—C21—C14	120.0 (3)
C8—C7—C6	117.8 (3)	N4—C21—C22	122.5 (2)
C8—C7—H7	121.1	C14—C21—C22	117.5 (3)
C6—C7—H7	121.1	C18—C22—C17	122.8 (2)
C7—C8—C9	121.2 (3)	C18—C22—C21	118.1 (2)
C7—C8—H8	119.4	C17—C22—C21	119.1 (2)
C5—N1—C1—C2	-1.1 (4)	N2—C10—C11—C12	177.2 (2)
ZN1—N1—C1—C2	-179.35 (19)	C9—C10—C11—C12	-2.8 (4)
N1—C1—C2—C3	1.0 (4)	N3—C11—C12—C13	-0.3 (4)
C1—C2—C3—C4	0.4 (4)	C10—C11—C12—C13	-179.6 (2)
C2—C3—C4—C5	-1.5 (4)	C11—C12—C13—C19	0.2 (4)
C1—N1—C5—C4	0.0 (3)	C21—C14—C15—C16	1.1 (5)
ZN1—N1—C5—C4	178.34 (19)	C14—C15—C16—C17	-0.8 (5)
C1—N1—C5—C6	-179.5 (2)	C15—C16—C17—C22	-0.4 (5)
ZN1—N1—C5—C6	-1.2 (3)	C21—N4—C19—C13	-177.6 (2)
C3—C4—C5—N1	1.3 (4)	C21—N4—C19—C20	1.3 (4)
C3—C4—C5—C6	-179.2 (2)	C12—C13—C19—N4	179.3 (2)
C10—N2—C6—C7	-0.1 (4)	C12—C13—C19—C20	0.3 (4)
ZN1—N2—C6—C7	176.6 (2)	C11—N3—C20—C18	-177.6 (2)
C10—N2—C6—C5	179.9 (2)	ZN1—N3—C20—C18	2.6 (3)
ZN1—N2—C6—C5	-3.3 (3)	C11—N3—C20—C19	0.5 (3)
N1—C5—C6—N2	2.9 (3)	ZN1—N3—C20—C19	-179.22 (17)
C4—C5—C6—N2	-176.6 (2)	C22—C18—C20—N3	178.1 (2)
N1—C5—C6—C7	-177.1 (3)	C22—C18—C20—C19	-0.1 (4)
C4—C5—C6—C7	3.4 (4)	N4—C19—C20—N3	-179.6 (2)
N2—C6—C7—C8	-0.9 (4)	C13—C19—C20—N3	-0.7 (3)
C5—C6—C7—C8	179.1 (3)	N4—C19—C20—C18	-1.4 (4)
C6—C7—C8—C9	0.8 (5)	C13—C19—C20—C18	177.5 (2)
C7—C8—C9—C10	0.2 (5)	C19—N4—C21—C14	-179.5 (2)
C6—N2—C10—C9	1.2 (4)	C19—N4—C21—C22	0.3 (4)
ZN1—N2—C10—C9	-175.60 (19)	C15—C14—C21—N4	179.6 (3)
C6—N2—C10—C11	-178.8 (2)	C15—C14—C21—C22	-0.3 (4)
ZN1—N2—C10—C11	4.5 (3)	C20—C18—C22—C17	-179.5 (2)
C8—C9—C10—N2	-1.2 (4)	C20—C18—C22—C21	1.6 (4)
C8—C9—C10—C11	178.7 (3)	C16—C17—C22—C18	-177.7 (3)
C20—N3—C11—C12	0.0 (3)	C16—C17—C22—C21	1.2 (4)
ZN1—N3—C11—C12	179.77 (18)	N4—C21—C22—C18	-1.8 (4)
C20—N3—C11—C10	179.3 (2)	C14—C21—C22—C18	178.1 (3)
ZN1—N3—C11—C10	-0.9 (3)	N4—C21—C22—C17	179.3 (2)
N2—C10—C11—N3	-2.2 (3)	C14—C21—C22—C17	-0.9 (4)
C9—C10—C11—N3	177.9 (2)		