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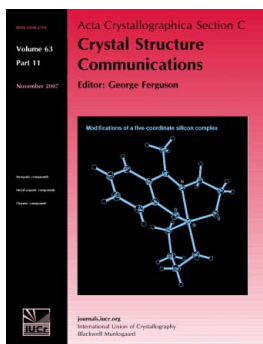
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A new polymorph of bis[2,6-bis(1H-benzimidazol-2-yl-κN³)pyridinido-κN]-zinc(II)

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The title compound, [Zn(C$_{19}$H$_{12}$N$_5$)$_2$], crystallizes in the tetragonal space group $P4_32_12$, with the monomer residing on a twofold axis. The imidazole N-bound H atoms are disordered over the two positions, with refined occupancies of 0.59 (3) and 0.41 (3). The strong similarities to, and slight differences from, a reported $P4_22_12$ polymorph which has a 50% smaller unit-cell volume [Harvey, Baggio, Muñoz & Baggio (2003). *Acta Cryst.* C**59**, m283–m285], to which the present structure bears a group–subgroup relationship, are discussed.

Comment

Metal complexes incorporating benzimidazole derivatives may mimic the behaviour of metal-ion sites in biological systems, in both structure and reactivity (Alagna *et al.*, 1984; Rijn *et al.*, 1987), and this fact has rendered their study increasingly attractive. One such derivative, namely 2,6-bis-(benzimidazol-2-yl)pyridine (BzimpyH$_2$), is a potentially active ligand which binds through one pyridine and two benzimidazole N atoms in a typical tridentate mode (a comprehensive review has been published recently; Boča *et al.*, 2011). In particular, a common pattern has two tridentate ligands bound to a transition metal cation (Tr), with the planar ligands at right angles to each other, thus shielding the cation from interaction with other species.

In these molecules, the ligand can appear as the neutral unit (BzimpyH$_2$), with both uncoordinated imidazole N atoms protonated, in which case there is a counter-ion balancing the [Tr(BzimpyH$_2$)$_2$]$^{2+}$ charge. Many structures of this sort appear in Version 5.33 of the Cambridge Structural Database (CSD; Allen, 2002), *viz.* DURWOJ (Huang *et al.*, 2010) and DUR-

WOJ01 (Wu, Huang, Yuan, Kou, Chen *et al.*, 2010) for Ni^{II}, EYINAB (Harvey *et al.*, 2004) for Zn^{II}, NETBUJ (Boca *et al.*, 1997) and PAFZIF (Ruttimann *et al.*, 1992) for Fe^{II}, and WUXBUN (Yan *et al.*, 2010), EZEXOX (Wu, Huang, Yuan, Kou, Jia *et al.*, 2010), OYAKEF (Guo *et al.*, 2011) and BAHJOL (Wu *et al.*, 2011) for Mn^{II}. There are also a number of complexes in which one of these H atoms is lost, giving a monoanion (hereinafter BzimpyH) which forms neutral Tr(BzimpyH)$_2$ units, *viz.* PANXAE (Shi *et al.*, 2003), PANXAE01 (Bai & Zhang, 2009) and TAWZOG (Rajan *et al.*, 1996) for Mn^{II}, TIBGUH (Zhang *et al.*, 2007) for Co^{II}, WICJOH (Wang *et al.*, 1994) and WICJOH01 (Yue *et al.*, 2006) for Cd^{II} (see footnote[1]), and EJEBOK (Harvey *et al.*, 2003) and EJEBOK01 (Yue *et al.*, 2006) for Zn^{II} (see footnote[1]).

(I)
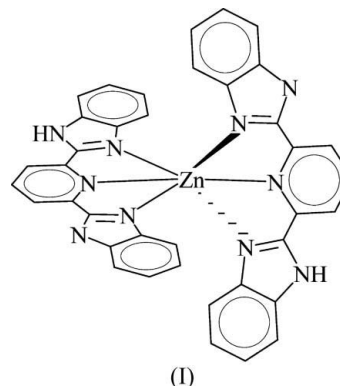
We present here the structure of the title complex, Zn(BzimpyH)$_2$, (I), where the ligand displays the latter behaviour. The compound appeared serendipitously in tiny amounts as a by-product of the frustrated synthesis of a Zn + BzimpyH$_2$ + tetrathionate complex (see *Experimental*). In addition to (I), the same crystallization batch produced a second, also unexpected, compound which proved to be a known polymorph of (I) [CSD refcode EJEBOK (Harvey *et*

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[1] CSD entry EJEBOK01 (Yue *et al.*, 2006) has been reported as a Zn^{II} structure with formula Zn(BzimpyH)$_2$, polymorphic with both EJEBOK (Harvey *et al.*, 2003) and the present complex, (I). In the same paper, the Cd isomorph is also reported (refcode WICJOH01). As reported for the Zn^{II} complex EJEBOK01 (Yue *et al.*, 2006), one of the two imidazole units in each BzimpyH$^-$ anion is assigned a fully occupied N-bound H atom. Examination of the crystal packing reveals a problem with the given assignment, since it produces an intermolecular N—H···H—N contact with H···H = 1.02 Å and N···N = 2.730 (13) Å. Furthermore, according to the published model, the two 'naked' imidazole N atoms make an intermolecular contact of 2.782 (14) Å, with no H atom between them. While a ΔF synthesis would be needed in order to assign the correct H-atom positions (the reflection data are not available), we think that a likely possibility is that the H atoms are distributed over all possible sites, with each short intermolecular imidazole N···N contact representing a hydrogen bond. Moreover, there is a further, more serious, objection to the structure as reported, observed in a bond-valence (BV) analysis (Brown, 2002). The BV calculation gives, for the reported Zn^{II} cation, a BV sum of 1.131 valence units (v.u.), quite outside the expected range for any 2+ cation (as a rule of thumb, ~2±0.025 v.u.), thus casting doubt on the cation assignment. If the metal is changed to Cd, the same calculation gives a BV sum of 2.164 v.u. In addition, the calculation for WICJOH01 (the Cd structure originally reported in the same paper) gives 2.190 v.u. for the central cation. The obvious explanation would be an erroneous cation assignment in the Zn case. These considerations advise against making comparisons using EJEBOK01, which has thus not been used in the present report. We do, however, use the apparently error-free Cd counterpart (refcode WICJOH01).

metal-organic compounds
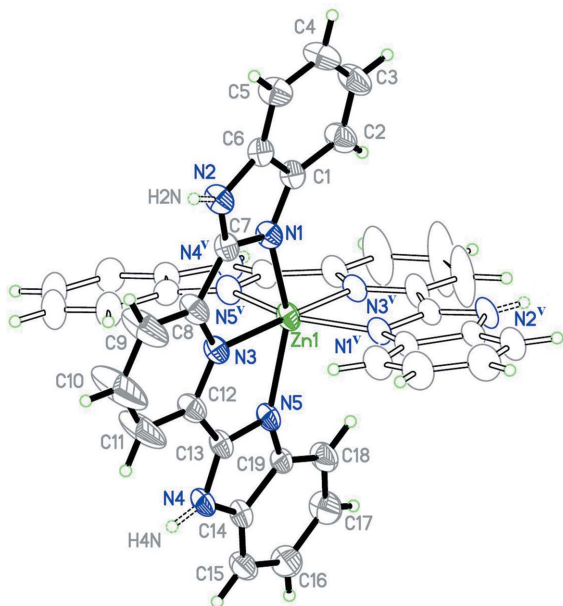
Figure 1
The molecular structure of (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 40% probability level. [Symmetry code: (v) $y + 1$, $x - 1$, $-z$.]

al., 2003), (II)], which presents a number of noteworthy similarities to (I) but some interesting differences as well.

Compound (I) crystallizes in the tetragonal space group $P4_32_12$ (No. 96), while (II) crystallizes in $P4_22_12$ (No. 94), although the *c* axis of (I) is doubled with respect to that of (II). The point group (422) is the same. There is a clear group–subgroup relationship, as $P4_32_12$ ($c' = 2c$) is a maximal non-isomorphic subgroup of $P4_22_12$. Unfortunately, the scant amount of material obtained precluded any serious attempt to detect any potential phase transition linking the two structures.

Table 1 presents a comparison of significant parameters in (I) and (II), while the slight differences introduced into the structure by symmetry relaxation will be presented below.

The structural building block in (I) is a $Zn(BzimpyH)_2$ monomer (Fig. 1) lying on a single twofold axis which traverses the Zn^{II} cation and relates the two N,N',N''-tridentate BzimpyH⁻ anions; thus, half of the molecule is independent. In the previously reported structure of (II), the monomer is bisected by a second independent twofold axis, passing through Zn^{II} but also bisecting the BzimpyH⁻ anion, thus rendering just one quarter of the monomer independent. In addition, in (II), there is a third symmetry-required twofold axis perpendicular to the other two diads. The symmetry differences between the two structures can be seen in Fig. 2, which shows a schematic representation of the symmetry elements at the origin in both space groups, where the molecules lie.

The BzimpyH⁻ anion in (I) is nearly planar, with a mean deviation of 0.063 (2) Å (maximum deviation for atom N5 of 0.1684 Å); the dihedral angle between the mean planes of the symmetry-related ligands is 75.7 (2)°, compared with an angle of 75.4 (3)° for (II). The similarities – metric as well as
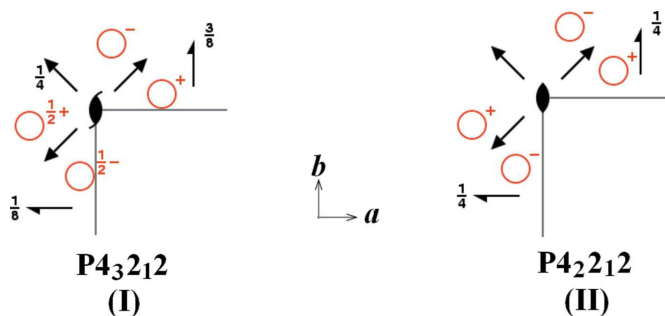
Figure 2
A schematic representation of the symmetry elements at the origin in space groups $P4_32_12$ (No. 96) for (I) and $P4_22_12$ (No. 94) for (II).

orientational – can be seen in Fig. 3, which shows an overlay of (I) and (II), with neither least-squares fitting nor rotations having been performed and with their relative original orientations in the unit cells preserved. The almost perfect overlap is apparent, with a mean unweighted deviation of 0.14 (8) Å for all atoms.

The double tridentate bite with five-membered chelate rings imposes a distorted geometry on the Zn coordination octahedron in (I), with '*cis*' N—Zn—N angles spanning the broad range 74.93 (7)–107.91 (7)° and '*trans*' angles spanning the range 141.35 (15)–173.98 (9)°. The strain in the ligand due to the triple (N,N',N'') bite is evidenced by the N1···N5 distance [4.220 (4) Å], which is significantly shorter than those reported for three (unstrained) free BzimpyH₂ entities (Freire *et al.*, 2003), which have a range of 4.550 (3)–4.580 (3) Å. Comparable values were observed for (II).

The Zn—N coordination distances also show the effect of symmetry relaxation (Table 1). Those in (II) are divided into two groups: Zn—N$_{central}$ and Zn—N$_{lateral}$. In (I), a very similar Zn—N$_{central}$ value is found, but the fourfold degeneracy of Zn—N$_{lateral}$ is broken, splitting into two groups. It is interesting to note that the average of these latter bond distances [2.1775 (14) Å] agrees fairly well with those in (II) [2.181 (3) Å].
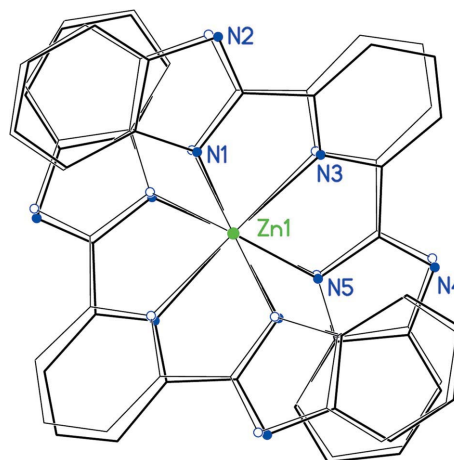
Figure 3
A common-origin orientation-preserving superposition of molecules (I) (heavy lines) and (II) (light lines).
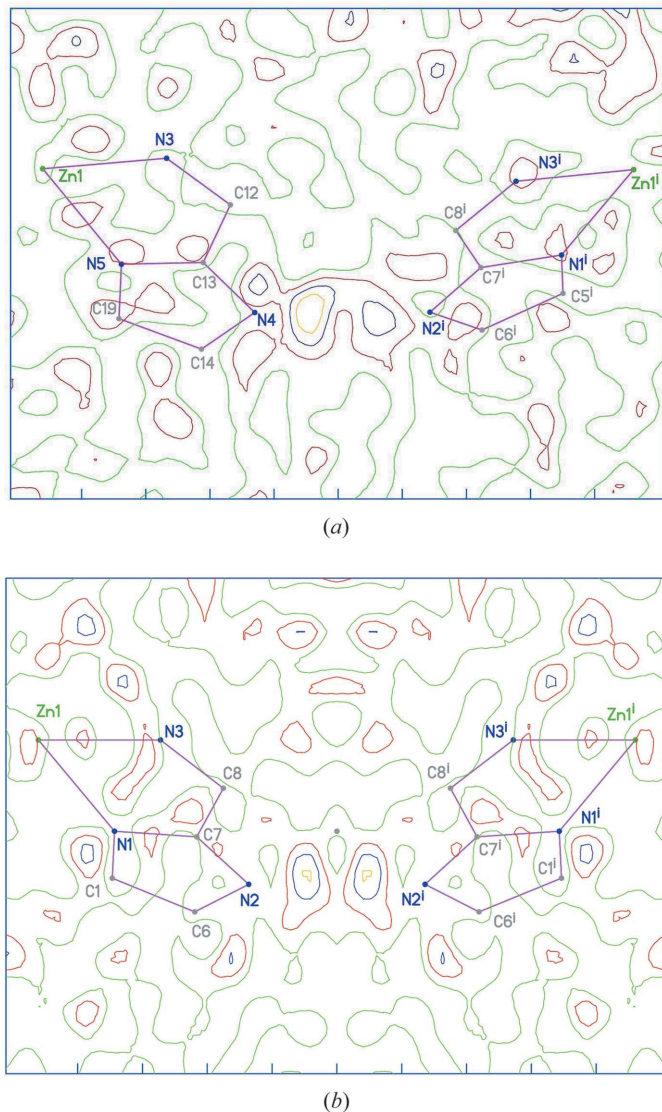
Figure 4
Difference maps for (a) (I) and (b) (II) (H atoms have been omitted from F_{calc}), showing the electron density in the neighbourhood of the imidazole N atoms. [Symmetry code: (i) $y + 1, x, -z$.]

The symmetry restrictions on the disordered imidazole N—H groups impose differences on the pattern of protonation. In the case of (II), the two N atoms per ligand which can be protonated are related by symmetry, so H-atom occupancy is forced to be 0.5 per N atom to give a total charge of −1 per ligand. In the case of (I), there are two independent N atoms to accommodate one or two H-atom sites in such a way that their populations sum to 1. In order to check for differences, ΔF syntheses were plotted in an orientation suitable for viewing the electron density in the neighbourhood of the imidazole N atoms (Fig. 4). The expected symmetric distribution in (II) contrasts with the asymmetric pattern in (I), notably biased towards atom N4. When allowed to refine, the occupancies reflected these results [0.59 (3) and 0.41 (3) for atoms N4 and N2, respectively]. These different disorder patterns for the imidazole H atoms are linked to the internal symmetry and surroundings of the molecule. There are
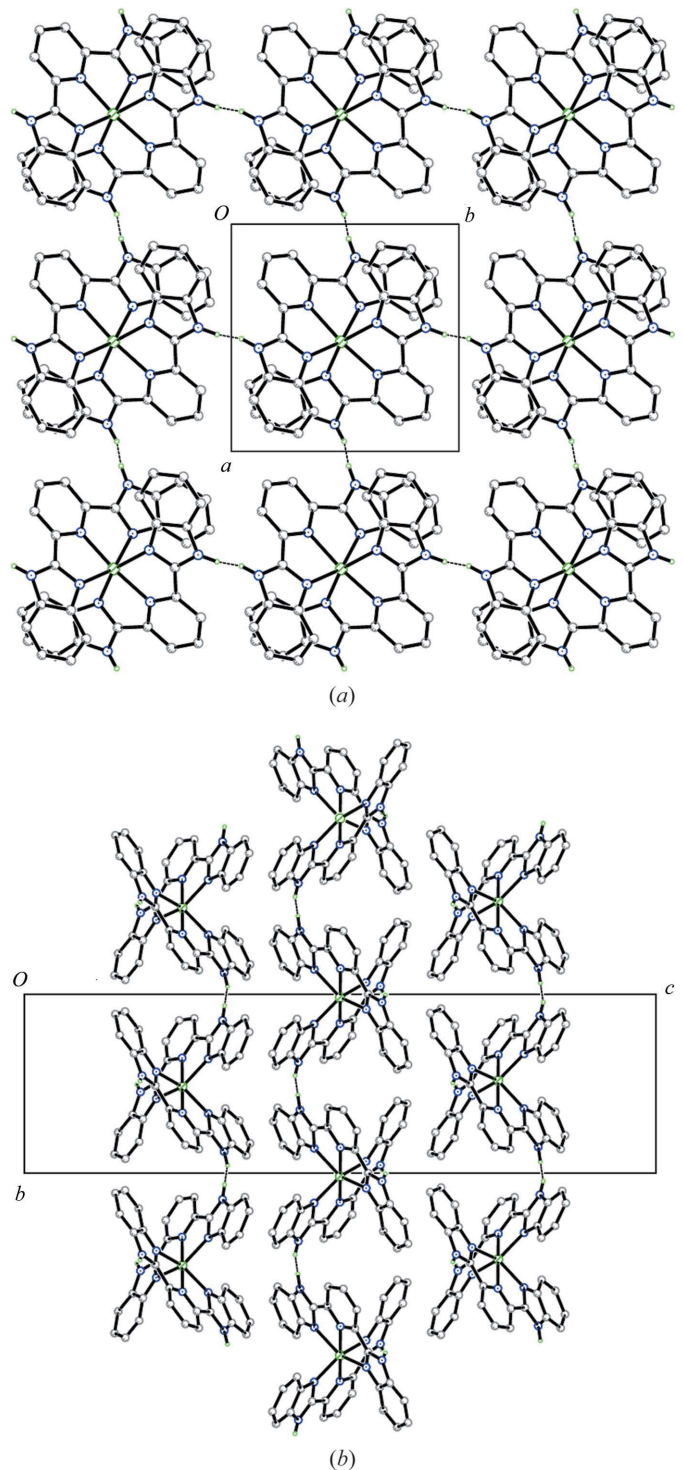
Figure 5
Packing views of (I). (a) A projection down [001], showing the two-dimensional structure mediated by strong N—H$\cdots$N hydrogen bonds. (b) A view along [010], showing the two-dimensional structures side-on.

examples in the literature (CSD refcode WICJOH01; Yue *et al.*, 2006) of Tr analogues with the monomers lying on general positions for which there is no disorder in the N—H groups, with one of the two imidazole N atoms fully protonated and the second 'naked' and acting as a hydrogen-bond acceptor. This leads to an ordered distribution of hydrogen bonds in

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space, defining a homogeneous three-dimensional hydrogen-bonded structure.

Entries 1 and 2 in Table 2 reflect the two different ways in which the disordered hydrogen bond in (I) is formed. The first entry corresponds to the major fraction, with the H atom linked to N4, while the second, minor, component has the H atom attached to N2. This contact links monomers in two (not three) directions parallel to the tetragonal base, to form broad two-dimensional nets on (001). Fig. 5(a) shows a packing view of one of these nets, while Fig. 5(b) presents a perpendicular view showing the way in which these planes stack. Interplanar interactions consist of much weaker C—H···π interactions (Table 2, entries 3 and 4). No π–π bonds linking aromatic groups are present in the structure, the rings being too far apart to have any kind of interaction.

A final difference observed between (I) and (II) is the enantiopurity revealed by the two refinements. While (II) refines with a Flack (1983) parameter of 0.48 (3), pointing to the presence of inversion twinning with almost equal populations of both absolute structures, (I) can be described as an almost enantiopure compound, with a Flack parameter of 0.087 (14).

As stated in the footnote, the analysis of a third Zn-(BzimpyH)$_2$ polymorph (CSD refcode EJEBOK01) has been published, but the structure as reported presents serious formal errors which mitigate against its use for detailed comparison. However, the fact that there is an isomorphous Cd complex (refcode WICJOH01) reported in the same work and apparently error-free might suggest that the analogous Zn complex does in fact exist, possibly with space group Cc, and with its Zn cation on a general position. This would be a nonsymmetric Zn(BzimpyH)$_2$ unit, metrically similar but different in crystallographic symmetry from the two variants discussed here. Unfortunately, for the time being this is only speculative and this (potentially interesting) comparison must be postponed until better data are available.

Experimental

In a frustrated attempt to obtain zinc tetrathionate [the main final product happened to be Zn(BzimpyH$_2$)(acetate) monohydrate], tiny amounts of pyramidal crystals of the title compound, (I), and bipyramidal crystals of the previously published polymorph, (II), were obtained.

An aqueous solution of zinc acetate dihydrate and potassium tetrathionate was allowed to diffuse slowly into a solution of BzimpyH$_2$ in dimethylformamide (DMF), with all solutions equimolar (0.080 M). After the intial formation of a solid conglomerate, spontaneous dissolution occurred. When the process seemed to have finished, the diffusion system was disassembled and the resulting solution allowed to evaporate slowly. On standing (for about three weeks), three different phases were present in different amounts, viz. an overwhelming majority of the main product, Zn(BzimpyH$_2$)-(C$_2$H$_3$O$_2$)$_2$·H$_2$O, and minor quantities of (I) and (II).

Crystal data (see Table 1)

Mo $K\alpha$ radiation
$\mu = 0.80$ mm^{-1}

0.42 × 0.38 × 0.38 mm

Table 1
Comparison of relevant data for (I) and (II).

Structure	(I)	(II)
Formula	[Zn(C$_{19}$H$_{12}$N$_5$)$_2$]	[Zn(C$_{19}$H$_{12}$N$_5$)$_2$]
M_r	686.04	686.04
Crystal system	Tetragonal	Tetragonal
Space group	$P4_32_12$	$P4_22_12$
a (Å)	9.7292 (2)	9.7411 (8)
c (Å)	34.3125 (13)	17.108 (2)
V (Å^3)	3247.93 (15)	1623.3 (3)
Z	4	2
T (K)	298	293
Flack parameter	0.087 (14)	0.48 (3)
Zn—N$_{central}$ (Å)	2.1054 (17) (2×)	2.088 (3) (2×)
Zn—N$_{lateral}$ (Å)	2.1319 (19) (2×), 2.2232 (19) (2×)	2.181 (3) (4×)

Table 2
Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the N4/C13/N5/C19/C14 and N1/C1/C6/N2/C7 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4N···N2^{i}	0.86	1.89	2.744 (3)	171
N2—H2N···N4^{ii}	0.86	1.94	2.744 (3)	156
C4—H4···Cg1^{iii}	0.93	2.94	3.579 (3)	127
C16—H16···Cg2^{iv}	0.93	2.94	3.633 (3)	132

Symmetry codes: (i) $y + 1, x, -z$; (ii) $y, x - 1, -z$; (iii) $y + \frac{1}{2}, -x + \frac{1}{2}, z + \frac{1}{4}$; (iv) $-y + \frac{3}{2}, x - \frac{1}{2}, z - \frac{1}{4}$.

Data collection

Oxford Gemini CCD S Ultra diffractometer	32522 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	3926 independent reflections
	3098 reflections with $I > 2\sigma(I)$
$T_{min} = 0.72$, $T_{max} = 0.74$	$R_{int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
$wR(F^2) = 0.090$	$\Delta\rho_{min} = -0.53$ e Å^{-3}
$S = 1.01$	Absolute structure: Flack (1983),
3926 reflections	with 1445 Friedel pairs
224 parameters	Flack parameter: 0.087 (14)
H-atom parameters constrained	

All H atoms were visible in a difference Fourier map. Those attached to C atoms were added at their expected positions (C—H = 0.93 Å) and allowed to ride. The single H atom of the BzimpyH$^-$ anion was found to be distributed unequally over the two potential sites at the N atoms of different imidazole units. Their locations were further idealized and their occupancies refined to final values of 0.59 (3) and 0.41 (3). In all cases, H-atom displacement parameters were assigned as U_{iso}(H) = 1.2U_{eq}(host). Similar to what was observed for polymorph (II), where H-atom disorder was present, the outermost part of the pyridine group presents elongated displacement ellipsoids normal to the plane of the ring, due either to genuine vibration or to an uncharacterized disorder.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to

prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3291). Services for accessing these data are described at the back of the journal.

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supplementary materials

A new polymorph of bis[2,6-bis(1*H*-benzimidazol-2-yl-*κN*³)pyridinido-*κN*]zinc(II)

Miguel Angel Harvey, Sebastián Suarez, Fabio Doctorovich and Ricardo Baggio

Bis[2,6-bis(1*H*-benzimidazol-2-yl- *κN*³)pyridinido-*κN*]zinc(II)

Crystal data

[Zn(C$_{19}$H$_{12}$N$_5$)$_2$]	D_x = 1.403 Mg m⁻³
M_r = 686.04	Mo $K\alpha$ radiation, λ = 0.71073 Å
Tetragonal, $P4_32_12$	Cell parameters from 12073 reflections
Hall symbol: P 4nw 2abw	θ = 3.5–28.5°
a = 9.7292 (2) Å	μ = 0.80 mm⁻¹
c = 34.3125 (13) Å	T = 298 K
V = 3247.93 (15) Å³	Pyramid, light yellow
Z = 4	0.42 × 0.38 × 0.38 mm
$F(000)$ = 1408	

Data collection

Oxford Gemini CCD S Ultra diffractometer	32522 measured reflections
	3926 independent reflections
Radiation source: fine-focus sealed tube	3098 reflections with $I > 2\sigma(I)$
Graphite monochromator	R_{int} = 0.041
ω scans, thick slices	θ_{max} = 28.5°, θ_{min} = 3.5°
Absorption correction: multi-scan	h = −12→12
(*CrysAlis PRO*; Oxford Diffraction, 2009)	k = −12→12
T_{min} = 0.72, T_{max} = 0.74	l = −45→46

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.038	H-atom parameters constrained
$wR(F^2)$ = 0.090	$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2]$
S = 1.01	where $P = (F_o^2 + 2F_c^2)/3$
3926 reflections	$(\Delta/\sigma)_{max} < 0.001$
224 parameters	$\Delta\rho_{max}$ = 0.28 e Å⁻³
0 restraints	$\Delta\rho_{min}$ = −0.53 e Å⁻³
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 1445 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.087 (14)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Zn1	0.98271 (2)	−0.01729 (2)	0.0000	0.03697 (13)	
N1	0.83297 (18)	−0.0840 (2)	0.04123 (6)	0.0372 (5)	
N2	0.62060 (19)	−0.0454 (2)	0.06625 (6)	0.0413 (5)	
H2N	0.5445	−0.0045	0.0715	0.050*	0.41 (3)
N3	0.83794 (17)	0.14354 (17)	0.00031 (6)	0.0355 (4)	
N4	1.0450 (2)	0.3536 (2)	−0.06371 (6)	0.0401 (5)	
H4N	1.0151	0.4360	−0.0670	0.048*	0.59 (3)
N5	1.06611 (19)	0.13871 (18)	−0.04101 (6)	0.0375 (5)	
C1	0.7945 (2)	−0.1981 (2)	0.06246 (7)	0.0369 (5)	
C2	0.8613 (3)	−0.3241 (3)	0.06830 (9)	0.0534 (8)	
H2	0.9475	−0.3417	0.0577	0.064*	
C3	0.7942 (3)	−0.4195 (3)	0.09027 (9)	0.0607 (8)	
H3	0.8350	−0.5049	0.0940	0.073*	
C4	0.6670 (3)	−0.3942 (3)	0.10730 (9)	0.0620 (8)	
H4	0.6269	−0.4613	0.1229	0.074*	
C5	0.5997 (3)	−0.2721 (3)	0.10152 (8)	0.0514 (7)	
H5	0.5140	−0.2560	0.1126	0.062*	
C6	0.6634 (2)	−0.1730 (3)	0.07851 (7)	0.0376 (6)	
C7	0.7243 (2)	0.0006 (2)	0.04428 (7)	0.0358 (6)	
C8	0.7289 (3)	0.1315 (3)	0.02333 (9)	0.0466 (6)	
C9	0.6348 (3)	0.2368 (3)	0.02616 (14)	0.1011 (16)	
H9	0.5580	0.2287	0.0421	0.121*	
C10	0.6571 (4)	0.3536 (4)	0.00489 (14)	0.144 (3)	
H10	0.5952	0.4261	0.0067	0.173*	
C11	0.7691 (4)	0.3655 (3)	−0.01895 (13)	0.0995 (15)	
H11	0.7838	0.4443	−0.0337	0.119*	
C12	0.8598 (3)	0.2562 (3)	−0.02037 (9)	0.0449 (6)	
C13	0.9892 (2)	0.2513 (2)	−0.04254 (7)	0.0373 (6)	
C14	1.1697 (3)	0.3048 (2)	−0.07661 (7)	0.0387 (6)	
C15	1.2722 (3)	0.3653 (3)	−0.09913 (8)	0.0499 (7)	
H15	1.2624	0.4536	−0.1091	0.060*	
C16	1.3887 (3)	0.2888 (3)	−0.10593 (9)	0.0591 (8)	
H16	1.4590	0.3259	−0.1210	0.071*	
C17	1.4037 (3)	0.1565 (3)	−0.09068 (9)	0.0612 (8)	
H17	1.4845	0.1084	−0.0954	0.073*	
C18	1.3024 (3)	0.0962 (3)	−0.06907 (9)	0.0510 (7)	
H18	1.3132	0.0079	−0.0592	0.061*	
C19	1.1823 (2)	0.1709 (2)	−0.06227 (7)	0.0355 (5)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03085 (14)	0.03085 (14)	0.0492 (2)	0.01051 (15)	0.00121 (9)	−0.00121 (9)
N1	0.0275 (10)	0.0369 (11)	0.0473 (12)	0.0087 (8)	−0.0009 (9)	0.0024 (9)
N2	0.0222 (9)	0.0405 (12)	0.0610 (14)	0.0074 (8)	0.0033 (9)	0.0051 (11)
N3	0.0269 (9)	0.0312 (10)	0.0484 (11)	0.0044 (7)	−0.0012 (10)	0.0008 (10)
N4	0.0394 (12)	0.0255 (9)	0.0552 (13)	0.0073 (9)	0.0028 (10)	0.0030 (9)
N5	0.0355 (10)	0.0261 (9)	0.0508 (12)	0.0072 (7)	0.0019 (9)	0.0003 (8)
C1	0.0276 (12)	0.0378 (13)	0.0452 (14)	0.0057 (9)	−0.0024 (10)	−0.0022 (11)
C2	0.0473 (17)	0.0458 (16)	0.067 (2)	0.0152 (14)	0.0016 (14)	0.0124 (14)
C3	0.0590 (18)	0.0420 (16)	0.081 (2)	0.0136 (14)	0.0057 (16)	0.0162 (15)
C4	0.0606 (19)	0.0528 (19)	0.073 (2)	0.0010 (14)	0.0037 (16)	0.0259 (16)
C5	0.0351 (14)	0.0566 (18)	0.0624 (19)	0.0006 (13)	0.0066 (13)	0.0117 (14)
C6	0.0276 (12)	0.0402 (14)	0.0450 (15)	0.0044 (10)	−0.0019 (11)	−0.0020 (11)
C7	0.0259 (10)	0.0357 (15)	0.0459 (14)	0.0070 (10)	−0.0005 (9)	−0.0023 (11)
C8	0.0314 (13)	0.0373 (14)	0.0712 (19)	0.0089 (10)	0.0092 (13)	0.0067 (13)
C9	0.063 (2)	0.062 (2)	0.179 (4)	0.0332 (17)	0.068 (3)	0.052 (2)
C10	0.096 (3)	0.080 (3)	0.257 (7)	0.065 (2)	0.103 (4)	0.088 (4)
C11	0.066 (2)	0.056 (2)	0.176 (4)	0.0362 (17)	0.050 (2)	0.058 (2)
C12	0.0372 (13)	0.0355 (14)	0.0619 (17)	0.0082 (11)	0.0021 (13)	0.0073 (12)
C13	0.0322 (14)	0.0274 (11)	0.0524 (15)	0.0034 (10)	0.0006 (11)	−0.0013 (10)
C14	0.0386 (14)	0.0281 (12)	0.0494 (16)	0.0029 (10)	0.0003 (12)	−0.0028 (11)
C15	0.0556 (17)	0.0330 (13)	0.0612 (19)	−0.0001 (13)	0.0090 (14)	0.0062 (13)
C16	0.0546 (18)	0.0545 (18)	0.068 (2)	0.0019 (15)	0.0234 (15)	0.0014 (15)
C17	0.0493 (18)	0.0579 (19)	0.076 (2)	0.0217 (15)	0.0202 (15)	0.0061 (16)
C18	0.0517 (16)	0.0386 (15)	0.0628 (19)	0.0139 (13)	0.0134 (14)	0.0044 (13)
C19	0.0399 (14)	0.0290 (12)	0.0375 (13)	0.0074 (9)	−0.0001 (11)	−0.0004 (10)

Geometric parameters (Å, º)

Zn1—N3[i]	2.1054 (17)	C4—C5	1.371 (4)
Zn1—N3	2.1054 (17)	C4—H4	0.9300
Zn1—N1[i]	2.1319 (19)	C5—C6	1.392 (4)
Zn1—N1	2.1319 (19)	C5—H5	0.9300
Zn1—N5[i]	2.2232 (19)	C7—C8	1.463 (3)
Zn1—N5	2.2232 (19)	C8—C9	1.378 (4)
N1—C7	1.344 (3)	C9—C10	1.368 (4)
N1—C1	1.379 (3)	C9—H9	0.9300
N2—C7	1.337 (3)	C10—C11	1.367 (4)
N2—C6	1.376 (3)	C10—H10	0.9300
N2—H2N	0.8600	C11—C12	1.382 (3)
N3—C12	1.323 (3)	C11—H11	0.9300
N3—C8	1.327 (3)	C12—C13	1.472 (3)
N4—C13	1.346 (3)	C14—C15	1.392 (4)
N4—C14	1.376 (3)	C14—C19	1.398 (3)
N4—H4N	0.8602	C15—C16	1.376 (4)
N5—C13	1.327 (3)	C15—H15	0.9300
N5—C19	1.381 (3)	C16—C17	1.396 (4)
C1—C2	1.402 (4)	C16—H16	0.9300

C1—C6	1.411 (3)	C17—C18	1.366 (4)
C2—C3	1.362 (4)	C17—H17	0.9300
C2—H2	0.9300	C18—C19	1.396 (3)
C3—C4	1.391 (4)	C18—H18	0.9300
C3—H3	0.9300		
N3ⁱ—Zn1—N3	173.98 (9)	C6—C5—H5	121.0
N3ⁱ—Zn1—N1ⁱ	76.46 (7)	N2—C6—C5	131.6 (2)
N3—Zn1—N1ⁱ	107.91 (7)	N2—C6—C1	108.1 (2)
N3ⁱ—Zn1—N1	107.91 (7)	C5—C6—C1	120.3 (2)
N3—Zn1—N1	76.46 (7)	N2—C7—N1	115.6 (2)
N1ⁱ—Zn1—N1	91.37 (11)	N2—C7—C8	126.3 (2)
N3ⁱ—Zn1—N5ⁱ	74.93 (7)	N1—C7—C8	118.1 (2)
N3—Zn1—N5ⁱ	100.50 (7)	N3—C8—C9	120.5 (2)
N1ⁱ—Zn1—N5ⁱ	151.33 (7)	N3—C8—C7	113.2 (2)
N1—Zn1—N5ⁱ	99.07 (8)	C9—C8—C7	126.3 (3)
N3ⁱ—Zn1—N5	100.50 (7)	C10—C9—C8	118.4 (3)
N3—Zn1—N5	74.93 (7)	C10—C9—H9	120.8
N1ⁱ—Zn1—N5	99.07 (8)	C8—C9—H9	120.8
N1—Zn1—N5	151.33 (7)	C11—C10—C9	121.0 (3)
N5ⁱ—Zn1—N5	84.40 (10)	C11—C10—H10	119.5
C7—N1—C1	103.79 (19)	C9—C10—H10	119.5
C7—N1—Zn1	113.74 (15)	C10—C11—C12	117.7 (3)
C1—N1—Zn1	141.35 (15)	C10—C11—H11	121.1
C7—N2—C6	104.26 (18)	C12—C11—H11	121.1
C7—N2—H2N	127.9	N3—C12—C11	121.1 (3)
C6—N2—H2N	127.9	N3—C12—C13	112.8 (2)
C12—N3—C8	121.4 (2)	C11—C12—C13	126.1 (3)
C12—N3—Zn1	120.38 (15)	N5—C13—N4	113.8 (2)
C8—N3—Zn1	118.14 (15)	N5—C13—C12	119.2 (2)
C13—N4—C14	105.90 (19)	N4—C13—C12	126.8 (2)
C13—N4—H4N	128.6	N4—C14—C15	131.6 (2)
C14—N4—H4N	125.3	N4—C14—C19	106.6 (2)
C13—N5—C19	104.67 (19)	C15—C14—C19	121.8 (2)
C13—N5—Zn1	112.50 (16)	C16—C15—C14	117.1 (2)
C19—N5—Zn1	141.97 (15)	C16—C15—H15	121.5
N1—C1—C2	130.8 (2)	C14—C15—H15	121.5
N1—C1—C6	108.2 (2)	C15—C16—C17	121.4 (3)
C2—C1—C6	121.0 (2)	C15—C16—H16	119.3
C3—C2—C1	116.9 (3)	C17—C16—H16	119.3
C3—C2—H2	121.6	C18—C17—C16	121.6 (3)
C1—C2—H2	121.6	C18—C17—H17	119.2
C2—C3—C4	122.6 (3)	C16—C17—H17	119.2
C2—C3—H3	118.7	C17—C18—C19	118.1 (2)
C4—C3—H3	118.7	C17—C18—H18	121.0
C5—C4—C3	121.2 (3)	C19—C18—H18	121.0
C5—C4—H4	119.4	N5—C19—C18	131.0 (2)
C3—C4—H4	119.4	N5—C19—C14	109.0 (2)
C4—C5—C6	118.0 (3)	C18—C19—C14	120.0 (2)

C4—C5—H5	121.0		
N3i—Zn1—N1—C7	179.79 (15)	Zn1—N1—C7—N2	172.31 (16)
N3—Zn1—N1—C7	4.10 (16)	C1—N1—C7—C8	−177.5 (2)
N1i—Zn1—N1—C7	−104.00 (17)	Zn1—N1—C7—C8	−6.9 (3)
N5i—Zn1—N1—C7	102.80 (17)	C12—N3—C8—C9	0.2 (4)
N5—Zn1—N1—C7	7.9 (2)	Zn1—N3—C8—C9	176.6 (3)
N3i—Zn1—N1—C1	−15.0 (3)	C12—N3—C8—C7	−178.9 (2)
N3—Zn1—N1—C1	169.3 (3)	Zn1—N3—C8—C7	−2.5 (3)
N1i—Zn1—N1—C1	61.2 (2)	N2—C7—C8—N3	−172.8 (2)
N5i—Zn1—N1—C1	−92.0 (3)	N1—C7—C8—N3	6.3 (3)
N5—Zn1—N1—C1	173.1 (2)	N2—C7—C8—C9	8.1 (5)
N1i—Zn1—N3—C12	−97.3 (2)	N1—C7—C8—C9	−172.7 (4)
N1—Zn1—N3—C12	175.7 (2)	N3—C8—C9—C10	−0.4 (6)
N5i—Zn1—N3—C12	78.8 (2)	C7—C8—C9—C10	178.7 (4)
N5—Zn1—N3—C12	−2.40 (19)	C8—C9—C10—C11	0.7 (7)
N1i—Zn1—N3—C8	86.30 (19)	C9—C10—C11—C12	−0.9 (7)
N1—Zn1—N3—C8	−0.72 (19)	C8—N3—C12—C11	−0.4 (4)
N5i—Zn1—N3—C8	−97.63 (19)	Zn1—N3—C12—C11	−176.7 (3)
N5—Zn1—N3—C8	−178.8 (2)	C8—N3—C12—C13	177.4 (2)
N3i—Zn1—N5—C13	−172.63 (16)	Zn1—N3—C12—C13	1.1 (3)
N3—Zn1—N5—C13	3.35 (16)	C10—C11—C12—N3	0.7 (6)
N1i—Zn1—N5—C13	109.58 (17)	C10—C11—C12—C13	−176.8 (4)
N1—Zn1—N5—C13	−0.4 (2)	C19—N5—C13—N4	1.1 (3)
N5i—Zn1—N5—C13	−99.12 (18)	Zn1—N5—C13—N4	172.92 (16)
N3i—Zn1—N5—C19	−5.6 (3)	C19—N5—C13—C12	−175.9 (2)
N3—Zn1—N5—C19	170.4 (3)	Zn1—N5—C13—C12	−4.1 (3)
N1i—Zn1—N5—C19	−83.3 (3)	C14—N4—C13—N5	−1.0 (3)
N1—Zn1—N5—C19	166.6 (2)	C14—N4—C13—C12	175.8 (2)
N5i—Zn1—N5—C19	68.0 (2)	N3—C12—C13—N5	2.2 (3)
C7—N1—C1—C2	176.0 (3)	C11—C12—C13—N5	179.9 (4)
Zn1—N1—C1—C2	9.9 (5)	N3—C12—C13—N4	−174.4 (2)
C7—N1—C1—C6	−1.9 (3)	C11—C12—C13—N4	3.3 (5)
Zn1—N1—C1—C6	−167.98 (19)	C13—N4—C14—C15	−179.1 (3)
N1—C1—C2—C3	−178.1 (3)	C13—N4—C14—C19	0.4 (3)
C6—C1—C2—C3	−0.5 (4)	N4—C14—C15—C16	177.9 (3)
C1—C2—C3—C4	−1.7 (5)	C19—C14—C15—C16	−1.6 (4)
C2—C3—C4—C5	2.5 (5)	C14—C15—C16—C17	−0.4 (5)
C3—C4—C5—C6	−1.0 (5)	C15—C16—C17—C18	1.4 (5)
C7—N2—C6—C5	−178.8 (3)	C16—C17—C18—C19	−0.3 (5)
C7—N2—C6—C1	−0.4 (3)	C13—N5—C19—C18	175.9 (3)
C4—C5—C6—N2	177.0 (3)	Zn1—N5—C19—C18	8.3 (5)
C4—C5—C6—C1	−1.2 (4)	C13—N5—C19—C14	−0.8 (3)
N1—C1—C6—N2	1.5 (3)	Zn1—N5—C19—C14	−168.45 (19)
C2—C1—C6—N2	−176.6 (2)	C17—C18—C19—N5	−178.1 (3)
N1—C1—C6—C5	−179.9 (2)	C17—C18—C19—C14	−1.6 (4)
C2—C1—C6—C5	2.0 (4)	N4—C14—C19—N5	0.2 (3)
C6—N2—C7—N1	−0.8 (3)	C15—C14—C19—N5	179.8 (2)

C6—N2—C7—C8	178.3 (2)	N4—C14—C19—C18	−176.9 (2)
C1—N1—C7—N2	1.7 (3)	C15—C14—C19—C18	2.7 (4)

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

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the N4/C13/N5/C19/C14 and N1/C1/C6/N2/C7 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4N···N2^{ii}	0.86	1.89	2.744 (3)	171
N2—H2N···N4^{iii}	0.86	1.94	2.744 (3)	156
C4—H4···Cg1^{iv}	0.93	2.94	3.579 (3)	127
C16—H16···Cg2^{v}	0.93	2.94	3.633 (3)	132

Symmetry codes: (ii) $y+1$, x, $-z$; (iii) y, $x-1$, $-z$; (iv) $y+1/2$, $-x+1/2$, $z+1/4$; (v) $-y+3/2$, $x-1/2$, $z-1/4$.

Comparison of relevant data for (I) and (II)

Structure	(I)	(II)
Formula	$C_{38}H_{24}N_{10}Zn$	$C_{38}H_{24}N_{10}Zn$
M_r	686.04	686.04
Crystal system	Tetragonal	Tetragonal
Space group	$P4_32_12$	$P4_22_12$
a (Å)	9.7292 (2)	9.7411 (8)
c (Å)	34.3125 (13)	17.108 (2)
V (Å^3)	3247.93 (16)	1623.3 (3)
Z	4	2
Flack parameter	0.087 (14)	0.48 (3)
Zn—N$_{central}$ (Å)	2.1054 (17) (2×)	2.088 (3) (2×)
Zn—N$_{lateral}$ (Å)	2.1319 (19) (2×), 2.2232 (19) (2×)	2.181 (3) (4×)