Bis[2,6-bis(1H-benzimidazol-2-yl-κN³)pyridinato-κN]zinc(II)

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The structure of $[Zn(C_{19}H_{12}N_5)_2]$, which is monomeric and consists of neutral $Zn(bbip-H)_2$ entities [bbip-H is the anionic form of bis(benzimidazolyl)pyridine, formed by the loss of one H atom], has been solved from a racemic twin. The Zn atom lies at a site with imposed 222 symmetry and the bbip-H ligand has imposed twofold symmetry. The imidazolyl H atom is disordered over two symmetry-related positions, thus raising the molecular symmetry as required by the space group. The angle between the planes of the two coordinated bbip-H ligands is 84.6 (3)°, so defining a distorted octahedral environment around the metal atom.

Comment

The fact that metal complexes with benzimidazole derivatives can mimic the behavior of metal ion sites in biological systems, both in structure and in reactivity (Sundberg & Martin, 1974; Hendriks *et al.*, 1982; Alagna *et al.*, 1984; Rijn *et al.*, 1987), has made the study of these complexes increasingly attractive. One of these derivatives with better coordination properties is 2,6-bis(benzimidazol-2-yl)pyridine, which can potentially act as a tridentate ligand through two benzimidazole and one pyridine N atom. In most of the metal complexes reported so far [15 entries in the November 2002 release of the Cambridge Structural Database (CSD); Allen, 2002], the group behaves as a neutral ligand (hereafter bbip), but in a few complexes, the group behaves as an anion (hereafter bbip-H) [*e.g.* Mn(bbip-H)₂, (II) (Rajan *et al.*, 1996), Cd(bbip-H)₂, (III) (Wang, Cui *et al.*, 1994), and Lu(bbip-H)(CH₄O)₂(NO₃)₂, (IV) (Wang, Zhu *et al.*, 1994)]. We present here a new Zn complex, Zn(bbip-H)₂, (I), in which the ligand displays this uncommon anionic behavior.

The building block of the structure is a Zn(bbip-H)₂ monomer. Because of the space-group symmetry, the asymmetric unit contains one-quarter of a molecule and there are

two molecules in the unit cell. The Zn cation lies at the origin, at the intersection of three twofold axes. The tridentate N,N',N''-bbip-H unit is bisected by one of the diads, thus rendering only half of the ligand independent, the rest being generated by symmetry (Fig. 1).

(I)
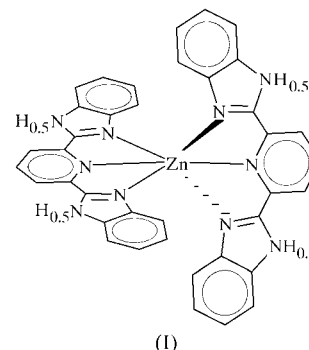
To make this situation compatible with the existence of a single nitrogen-bound H atom, there are only two possible options; either the H atom is ordered and occupies a special position on the twofold axis, midway between two symmetry-related N atoms (which share the H atom in a symmetric $N\cdots H\cdots N$ interaction), or the H atom is bonded to only one of the two otherwise equivalent N atoms, in a disordered fashion. In this case, the average image would be that of a double half H atom at each side of the diad. Both models were analyzed using least-squares refinement. The first model, with an H atom on the twofold axis, 1.37 Å from each N atom, resulted in a large displacement parameter for the H atom ($\sim$0.15 Å^2). The second option converged giving a reasonable H-atom position, $\sim$0.78 Å from atom N3, with a normal displacement parameter, so the disordered model was used in the subsequent refinement. This disorder was not the only anomaly present in the structure; the model also had to be refined as a racemic twin, and the effects of this special kind of disorder are manifested in unusually large displacement parameters for atoms C9 and C10.

In the bbip-H unit, the most significant departure from planarity is the dihedral angle of 5.5 (1)° between the lateral imidazolyl planes [mean deviation = 0.015 (3) Å] and the plane of the central pyridine ring [mean deviation = 0.001 (1) Å]. Hydrogen-bonding interactions (Table 2), in turn, push the two coordinated bbip-H ligands towards each other, the dihedral angle between their planes being 84.6 (3)° and that between neighboring imidazolyl groups being 69.7 (1)°. The strain imposed by coordination is apparent in the distorted geometry of the Zn octahedron, in which the angles that ideally would be right angles are actually in the range 75.91 (7)–104.09 (7)°, and opposite N atoms subtend angles of 151.83 (14) and 180.00 (17)° to the cation (Table 1). Evidence of this strain can also be found in the bbip-H molecular geometry, since the $N\cdots N$ distance between the outermost coordinated N atoms [4.231 (6) Å] is shorter than the equivalent distance in non-coordinated bbip. In the three unstrained moieties reported by Freire *et al.* (2003), this separation is larger [4.550 (3)–4.580 (3) Å], irrespective of the presence or absence of strong hydrogen-bonding interactions.

However, since the free ligand crystallizes with its two protonated N atoms pointing inwards, in a *cis* mode, any eventual N—N⋯H—N repulsion might tend to 'open' the molecular skeleton, thus impairing this comparison. Nevertheless, the non-interacting H⋯H distances found in free bbip (> 3 Å) suggest that the comparison is reasonable.

The charged character of bbip-H does not specifically seem to favor coordination to the positive cation, which is reported to happen, for example, in (III). In the present case, the $Zn-N$ coordination distances [$Zn-N_{py}$ = 2.090 (3) Å (× 2) and $Zn-N_{benzimid}$ = 2.181 (3) Å (× 4)] are almost identical to those found in similarly coordinated ZnN_6 cores with tridentate neutral ligands [the average values for eight ligands in four structures found in the CSD are $\langle Zn-N_{central}\rangle$ = 2.076 (11) Å and $\langle Zn-N_{lateral}\rangle$ = 2.187 (20) Å] and share the typical marked difference in bonding distances for the two types of coordinated N atoms.

The $Zn(bbip-H)_2$ molecular entity is neutral, as the ligand behaves as an anion, thus balancing the charge on the cation. This situation has already been observed in the homologous Mn, (II), and Cd, (III), complexes of bbip-H, although there are some structural differences; in (II) and (III), there is no disorder and the hydrogen-bond interactions are distributed evenly in space, defining a homogeneous three-dimensional hydrogen-bonded structure. The hydrogen bonding in (II) and (III) is restricted to the linking of monomers in two directions perpendicular to [001], in order to form broad two-dimensional structures parallel to the (001) plane. Fig. 2 shows a packing view of (I), in which these 'planes' can be seen in projection as broad horizontal 'strips', at heights of $z = 0, \frac{1}{2}$ and 1. The resulting two-dimensional supramolecular arrangements are not directly connected and interact with one
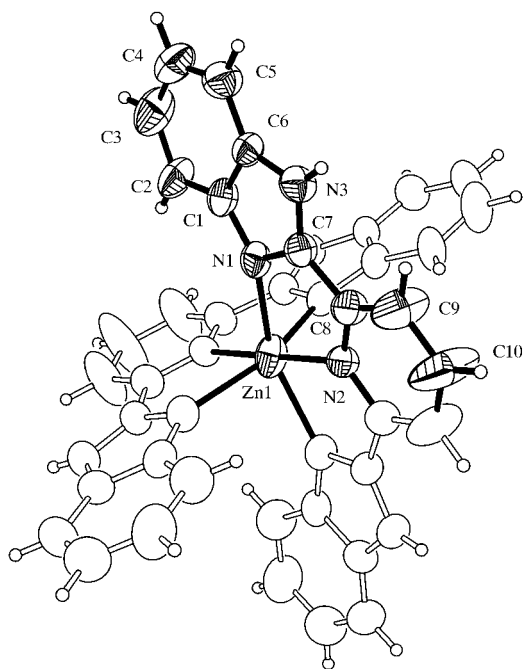

Figure 2
A view of the crystal packing, showing how the (disordered) hydrogen bonds build two-dimensional supramolecular arrays parallel to (001). Channels nearly parallel to the projection direction are clearly visible. Benzimidazole H atoms have been omitted for clarity.

another through much weaker forces. Inspection of Fig. 2 also reveals that the coordination polyhedra look like 'crosses' when projected along [110] and [$\bar{1}$10], and the parallel stacking along the view directions determines well defined channels, ~4 Å in diameter, as estimated by a simple 'point-atom' approximation.

The coordination geometry and the packing interactions result in the aromatic groups being too far from one another to allow any kind of π interaction between them.

Experimental

Figure 1
An *XP* plot (Sheldrick, 1994) of the Zn coordination polyhedron in (I), with the crystallographically independent part of the molecule represented by highlighted displacement ellipsoids (40% probability level).
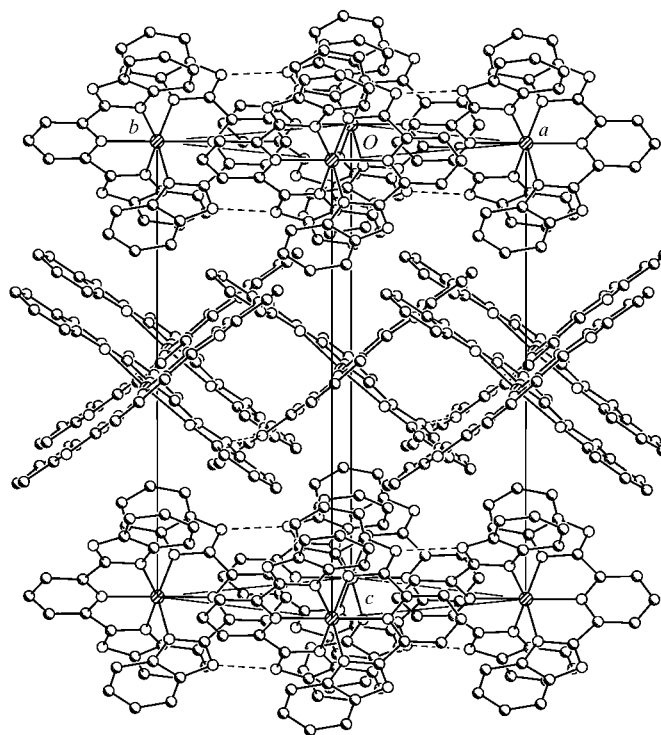
Crystal data

$[Zn(C_{19}H_{12}N_5)_2]$	Mo $K\alpha$ radiation
M_r = 686.04	Cell parameters from 84
Tetragonal, $P4_22_12$	reflections
a = 9.7411 (8) Å	θ = 3.7–24.5°
c = 17.108 (2) Å	μ = 0.80 mm^{-1}
V = 1623.3 (3) Å^3	T = 293 (2) K
Z = 2	Square bipyramid, colorless
D_x = 1.404 Mg m^{-3}	0.22 × 0.12 × 0.12 mm

Data collection

Bruker CCD area-detector diffractometer	1866 independent reflections
φ and ω scans	778 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1996)	$R_{int} = 0.071$
	$\theta_{max} = 28.0°$
$T_{min} = 0.86$, $T_{max} = 0.89$	$h = -12 \rightarrow 11$
9552 measured reflections	$k = -6 \rightarrow 12$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{max} = 0.002$
$S = 0.86$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
1866 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
118 parameters	Absolute structure: Flack (1983), 663 Friedel pairs
H atoms treated by a mixture of independent and constrained refinement	Flack parameter = 0.48 (3)

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	2.090 (3)	C1—C6	1.406 (5)
Zn1—N1	2.181 (3)	C2—C3	1.380 (5)
N1—C7	1.340 (4)	C3—C4	1.379 (6)
N1—C1	1.380 (4)	C4—C5	1.373 (4)
N2—C8	1.325 (3)	C5—C6	1.396 (5)
N3—C7	1.338 (4)	C7—C8	1.464 (5)
N3—C6	1.366 (4)	C8—C9	1.378 (4)
C1—C2	1.392 (5)	C9—C10	1.372 (4)
N2—Zn1—N2^i	180	N1—Zn1—N1^i	99.76 (14)
N2—Zn1—N1	75.91 (7)	N1—Zn1—N1^{iii}	87.07 (13)
N1^{ii}—Zn1—N1	151.83 (14)		

Symmetry codes: (i) $-x, -y, z$; (ii) $-y, -x, -z$; (iii) $y, x, -z$.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3N⋯N3^{iv}	0.78 (4)	2.01 (3)	2.761 (6)	162 (5)

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

H atoms attached to C atoms were placed in idealized positions and allowed to ride on their parent atoms. The H atom on the protonated N atom in bbip-H was found in a difference Fourier map, very close to a twofold axis, and was refined using an isotropic displacement parameter with a split disordered model (50% occupancy at 0.78 Å from each of the two non-coordinated benzimidazole N atoms). The final structural model was refined as a racemic twin, resulting in almost equal populations [48 (3)/52 (3)%].

Data collection: *SMART–NT* (Bruker, 2001); cell refinement: *SMART–NT*; data reduction: *SAINT–NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

References

Alagna, L., Hassnain, S. S., Piggott, B. & Williams, D. J. (1984). *Biochem. J.* **59**, 591–595.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (2000). *SAINT–NT*. Version 6.02a. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Bruker (2001). *SMART–NT*. Version 5.624. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Freire, E., Baggio, S., Muñoz, J. C. & Baggio, R. (2003). *Acta Cryst.* C**59**, o259–o262.
Hendriks, H. M. J., Birker, P. J. M. W. L., Verschoor, G. C. & Reedijk, J. (1982). *J. Chem. Soc. Dalton Trans.* pp. 623–631.
Rajan, R., Rajaram, R., Nair, B. U., Ramasami, T. & Mandal, S. K. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2019–2021.
Rijn, J. V., Reedijk, J., Dartmann, M. & Krebs, B. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2579–2593.
Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Sundberg, R. J. & Martin, R. B. (1974). *Chem. Rev.* **74**, 471–517.
Wang, J., Zhu, Y., Wang, S., Gao, Y. & Shi, Q. (1994). *Polyhedron*, **13**, 1405–1409.
Wang, S., Cui, Y., Tan, R., Luo, Q., Shi, J. & Wu, Q. (1994). *Polyhedron*, **13**, 1661–1668.