

Di- μ -azido-bis[[1-(2-pyridylmethyl- iminomethyl)-2-naphtholato]zinc(II)]

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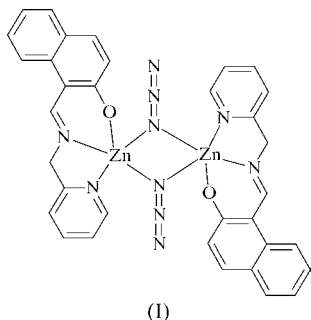
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The title compound, $[\text{Zn}_2(\text{C}_{17}\text{H}_{13}\text{N}_2\text{O})_2(\text{N}_3)_2]$, is an azide-bridged dinuclear zinc(II) complex which has inversion symmetry. The Zn^{II} atom is five-coordinated in a square-pyramidal configuration by one O and two N atoms of one Schiff base ligand [$\text{Zn}-\text{O} = 1.902(2) \text{ \AA}$ and $\text{Zn}-\text{N} = 1.938(2)$ and $2.002(2) \text{ \AA}$] and by one terminal N atom [$\text{Zn}-\text{N} = 1.985(2) \text{ \AA}$] of a bridging azide ligand defining the basal plane, and by another terminal N atom of another bridging azide ligand [$\text{Zn}-\text{N} = 2.554(2) \text{ \AA}$] occupying the apical position.

Comment

Metal-organic complexes containing bridging ligands are of current interest because of their interesting molecular topologies and crystal-packing motifs, as well as the fact that they may be designed with specific functionalities (Supriya *et al.*, 2005; Batten & Robson, 1998; Colacio *et al.*, 2005; Abourahma *et al.*, 2002; Konar *et al.*, 2002). In addition to being robust and thermally stable, some possess photoluminescent properties, a feature that has contributed to d^{10} metal polynuclear complexes being investigated in the search for new materials (Weidenbruch *et al.*, 1989; Kunkely & Vogler, 1990; Bertinello *et al.*, 1992). Among the Zn^{II} and Cd^{II} complexes of this class, most possess photoluminescent properties (Sang & Xu, 2005; Wang *et al.*, 2003).



Due to the versatile coordination modes of the ambidentate azide ligand, this pseudohalide ligand has become one of the

most extensively studied building blocks in the field of polynuclear complexes (Woodward *et al.*, 2005; Mukherjee *et al.*, 2001; Goher *et al.*, 2002). A major obstacle to a more comprehensive study of such azide-based complexes is the lack of rational synthetic procedures since, with the present state of knowledge, it is hardly possible to determine which coordination mode will be adopted by the azide ligand and whether the sought after alternating chain structure will finally be formed (Tercero *et al.*, 2002; Ribas *et al.*, 1999; Liu *et al.*, 2003).

Our work is aimed at obtaining polynuclear complexes. Based on the above considerations, the author has already reported an azide-bridged polynuclear copper(II) complex, *viz.* *catena*-poly[[{4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenolato}copper(II)]- μ -azido], $[\text{Cu}(\text{bdmp})(\text{N}_3)]_n$, (II) (You, 2005). In (II), the bridging azide ligand coordinates to two metal atoms *via* the same terminal N atom. The $\text{Cu}(\text{bdmp})$ moieties are linked by the bridging azide ligands, forming polymeric chains. In order to study the effects of Schiff base ligands in the construction of polynuclear complexes with the azide ligand, we have designed and synthesized a rigid tridentate ligand, *viz.* 1-(2-pyridylmethyliminomethyl)-2-naphthol (Hpmmn), which is different from the flexible tridentate ligand 4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenol (Hbdmp) used in the preparation of (II). The title complex, $[\text{Zn}_2(\text{pmmn})_2(\text{N}_3)_2]$, (I), formed by the reaction of Hpmmn, sodium azide and zinc(II) acetate, is reported here.

Complex (I) is an azide-bridged dinuclear zinc(II) compound (Fig. 1) which has inversion symmetry. The Zn^{II} atom is in a square-pyramidal coordination, with atoms O1, N1 and N2 of the pmmn ligand and the terminal N atom (N3) of a bridging azide ligand defining the basal plane, and one terminal N atom [$\text{N}3^{\dagger}$; symmetry code: (i) $1 - x, -y, 1 - z$] of another bridging azide ligand occupying the apical position. These are similar to the coordination modes of the Schiff base ligand and the bridging azide anion observed in (II). However, (I) and (II) are dinuclear and polynuclear complexes, respectively. This difference between the two structures is very

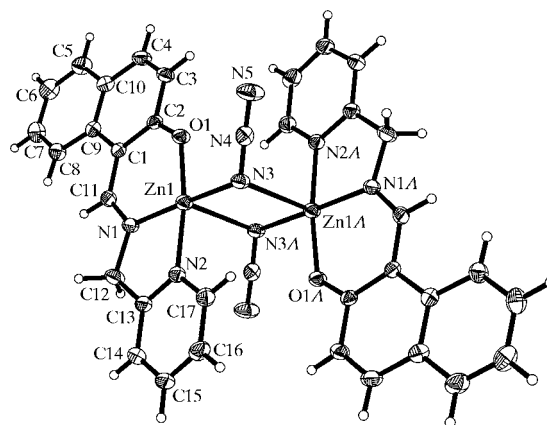


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A or left unlabelled are at the symmetry position $(1 - x, -y, 1 - z)$.

likely caused by the hindrance effects of the Schiff bases. In (I), the rigid pmmn ligand is kept almost coplanar when coordinated to the metal ions, with a mean deviation from the plane of 0.057 (3) Å. The basal least-squares planes of the two adjacent Zn^{II} centres are parallel to each other, making it possible for the two azide anions to be coordinated to the same two Zn^{II} atoms. In contrast, in (II), the bdmf is a flexible Schiff base ligand. The basal least-squares planes of the two adjacent Cu^{II} centres in (II) are not parallel to each other and form a dihedral angle of 43.5 (2)°. This orientation makes it difficult for the other azide ligand to coordinate to the same two metal atoms as the first azide ligand from the other side. However, the other bridging azide has no choice but to coordinate to the third metal atom *via* the low-hindrance side of (II). Thus, complex (II) forms an infinite chain structure. The bond lengths around the metal centre are comparable in (I) and (II), although the metal centres are Zn^{II} and Cu^{II}, respectively. The different configurations lead to an *M*–*N*–*M* bond angle of 95.44 (10)° in (I), much smaller than the corresponding value of 129.1 (2)° observed in (II), and the *M*···*M* distance in (I) of 3.380 (2) Å is much shorter than the corresponding value of 4.196 (2) Å in (II).

The bond lengths subtended at atom Zn1 in the basal plane are comparable with those observed in other Schiff base zinc(II) complexes (Gross & Vahrenkamp, 2005; Chen *et al.*, 2005) and, as expected, the bond involving pyridine atom N2 [2.003 (2) Å] is longer than that involving imine atom N1 [1.938 (2) Å] (Mondal *et al.*, 2001). The bridging azide group is nearly linear and shows bent coordination modes with the metal atoms (Table 1).

Experimental

2-Hydroxy-1-naphthaldehyde (0.1 mmol, 17.2 mg) and 2-aminomethylpyridine (0.1 mmol, 10.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a yellow solution. To this solution was added an aqueous solution (3 ml) of NaN₃ (0.1 mmol, 6.5 mg) and an MeOH solution (5 ml) of Zn(CH₃COO)₂·4H₂O (0.1 mmol, 25.6 mg), with stirring. The mixture was stirred for another 10 min at room temperature. After keeping the filtrate in air for 17 d, colourless block-shaped crystals of (I) were formed (yield 72.3%, based on the Schiff base used).

Crystal data

[Zn ₂ (C ₁₇ H ₁₃ N ₂ O) ₂ (N ₃) ₂]	<i>D</i> _x = 1.600 Mg m ⁻³
<i>M</i> _r = 737.39	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Cell parameters from 2253 reflections
<i>a</i> = 7.587 (1) Å	<i>θ</i> = 2.7–23.4°
<i>b</i> = 14.746 (2) Å	<i>μ</i> = 1.62 mm ⁻¹
<i>c</i> = 13.692 (2) Å	<i>T</i> = 298 (2) K
<i>β</i> = 92.53 (2)°	Block, colourless
<i>V</i> = 1530.3 (4) Å ³	0.25 × 0.21 × 0.17 mm
<i>Z</i> = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	3406 independent reflections
<i>ω</i> scans	2491 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.031
<i>T</i> _{min} = 0.688, <i>T</i> _{max} = 0.770	<i>θ</i> _{max} = 27.5°
8467 measured reflections	<i>h</i> = -9 → 9
	<i>k</i> = -19 → 13
	<i>l</i> = -17 → 15

Table 1
Selected geometric parameters (Å, °).

Zn1–O1	1.902 (2)	Zn1–N3	1.985 (2)
Zn1–N1	1.938 (2)	Zn1–N3 ⁱ	2.554 (2)
Zn1–N2	2.003 (2)		
O1–Zn1–N1	91.89 (10)	N1–Zn1–N3 ⁱ	97.94 (11)
O1–Zn1–N3	91.30 (10)	N2–Zn1–N3 ⁱ	91.17 (11)
N1–Zn1–N3	175.74 (10)	N3–Zn1–N3 ⁱ	84.56 (11)
O1–Zn1–N2	172.02 (10)	Zn1–N3–Zn1 ⁱ	95.44 (10)
N1–Zn1–N2	82.55 (10)	N4–N3–Zn1	120.6 (2)
N3–Zn1–N2	93.98 (11)	N4–N3–Zn1 ⁱ	112.9 (2)
O1–Zn1–N3 ⁱ	95.28 (10)	N5–N4–N3	177.1 (3)

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

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.120$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.03	$\Delta\rho_{max} = 0.55 \text{ e } \text{Å}^{-3}$
3406 reflections	$\Delta\rho_{min} = -0.25 \text{ e } \text{Å}^{-3}$
217 parameters	
H-atom parameters constrained	

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C–H distances in the range 0.93–0.97 Å and with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1242). Services for accessing these data are described at the back of the journal.

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