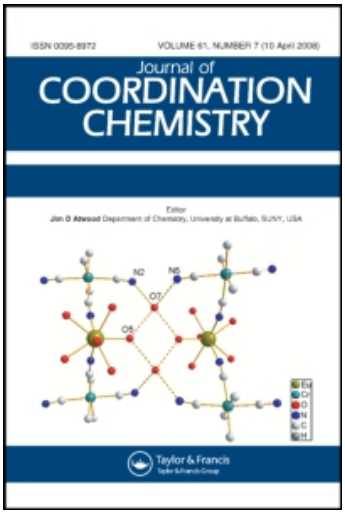

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CONSTRUCTION OF A SELF-ASSEMBLING, NEUTRAL, TWO-DIMENSIONAL STRUCTURE WITH A π-π STACKED COLUMN: $Zn(N_3)_2(4,4'\text{-BIPY})$

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CONSTRUCTION OF A SELF-ASSEMBLING, NEUTRAL, TWO-DIMENSIONAL STRUCTURE WITH A $\pi-\pi$ STACKED COLUMN: $Zn(N_3)_2(4,4'\text{-BIPY})$

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A room temperature single-crystal X-ray structure determination of $Zn(N_3)_2$bpy (bpy = 4,4′-bipyridyl) shows it to be a porous structure, comprised of parallel one-dimensional $\cdots Zn(\mu\text{-}N_3)_2Zn(\mu\text{-}N_3)_2Zn\cdots$ chains, the zinc atoms cross linked in the second dimension by bridging bpy ligands. Crystals are monoclinic, $C2/m$, $Z=2$, $a=16.000(2)$, $b=11.442(1)$, $c=11.272(1)$ Å, $\beta=120.75(1)°$, conventional R on $|F|$ being 0.040 for 1576 independent observed ($I>2\sigma(I)$) reflections. The zinc/azide chain is an interesting combination of bridging types, incorporating ZnN_2Zn four-membered rings in which the azides bridge through one terminal atom, and six-membered rings in which one of the azides coordinates to a pair of zinc atoms in end-on fashion.

Keywords: Zinc(II); X-ray structure; azide; 4,4′-bipyridyl

INTRODUCTION

Self-assembled aggregates with unusual physical properties[1] involving π-stacking have offered promise of accessing interesting arrays.[2,3] The potentially ambidentate azide ligand offers differing modes of bridging pairs of metal atoms by $M(\mu\text{-}N_3)_2M$ rings of two types in which it may be end-on (EO) (M···M typically 5.2–5.3 Å)[4,1(b)] and end-to-end (EE) (M···M 3.2–3.5 Å)[4,5] (Scheme 1). Metal atoms thus linked offer the possibility of further linkage by way of vacant coordination sites with other bifunctional 'rods' or

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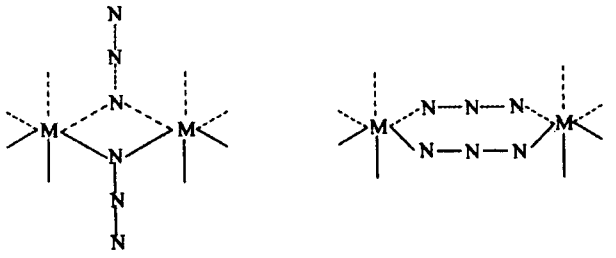

end on *end to end*

SCHEME 1

'spacers' such as 4,4′-bipyridyl (bpy) utilized previously in producing motifs such as interpenetrating square grid sheets,[6(a)] porous solids,[6(b)] T-shaped motifs,[6(c),(d)] two-dimensional square networks,[6(e),(f)] and trigonal planar arrays with large rectangles.[6(g)] With these possibilities in mind we have reacted solutions of zinc(II) azide with bpy, obtaining a novel neutral two-dimensional array of $Zn(N_3)_2$: bpy (1 : 1), characterized by a room-temperature single-crystal X-ray study, reported herein.

EXPERIMENTAL

Synthesis

The compound was synthesized by the addition of aqueous sodium azide (0.52 g, 8 mmol, 20 cm^3 to 4,4′-bipyridyl (0.97 g, 4 mmol) in ethanol (30 cm^3). The white crystalline solid, was washed with water (3 × 20 cm^3) and ethanol (3 × 20 cm^3) and dried at 60°C; yield 1.0 g (82%). Crystals suitable for X-ray work were obtained by diffusion of sodium azide (0.2 M) and 4,4′-bipyridyl (0.1 M) in aqueous ethanol (1 : 1), tabular colourless crystals being obtained after a few days at the ethanol/glycol interface. Found: C, 39.4; H, 2.6; $C_{10}H_8N_8Zn$ requires: C, 39.29; H, 2.62%. In the azide region of the IR spectrum, bands were observed at 2094(s) and 2060(s) cm^{-1} (KBr pellet).

Structure Determination

A unique room temperature four-circle diffractometer data set was measured ($2\theta_{max}$ 54°, ω-scan mode; graphite-monochromatized MoKα radiation, $\lambda = 0.71069$ Å; ENTAF-Nonius CAD-4 instrument; $T = 295$ K)

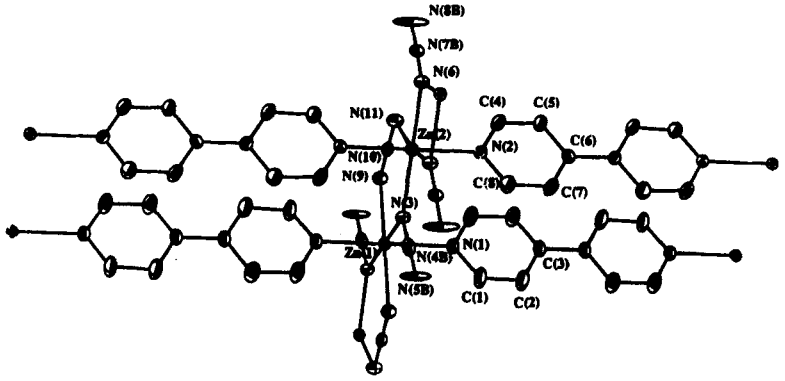

FIGURE 1 A perspective drawing of $[Zn(N_3)_2(4,4'\text{-bipy})]_\infty$; non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 30% of electron density, hydrogen atoms omitted for clarity.

yielding 2061 independent reflections, 1576 with $I > 2\sigma(I)$ being considered observed and used in full-matrix least-squares refinement after empirical (ψ-scan) absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms (Figure 1, Table I); $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ at convergence were $R = 0.040$, $R_w = 0.047$, $S = 1.09$. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

Although the asymmetric unit of the structure is a single 1 : 1 formula unit, there are two independent zinc atoms. Both lie in the crystallographic mirror plane at $y = 0$ normal to the two-fold axis (b), together with all atoms of the azide anions, pairs of which link them into a one-dimensional array along c, and occupy in each case four of the coordination sites about each zinc in the plane (Figure 2). The fifth and sixth coordination sites are occupied by symmetry-related pairs of bpy nitrogen atoms, the second ring of each bpy being generated from the first by the mirror plane at $y = \pm 0.5$ and spacing each zinc atom from its counterparts related by the unit b translation, (11.442(1) Å), to form a porous, two-dimensional polymeric sheet. Zn(1) and its associated bpy ligands have additional symmetry, Zn(1) lying also on the crystallographic 2 axis at the origin, site symmetry $2/m$ ($= i$), the crystallographic axis also coincident with the long axis of the

TABLE I Atomic coordinates and equivalent isotropic thermal parameters

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Zn(1)	0	0	0	1.91(3)
Zn(2)	−0.02561(4)	0	0.33680(6)	1.88(2)
N(1)	0	0.1895(4)	0	2.2(2)
N(2)	−0.0329(2)	0.1899(3)	0.3214(3)	2.2(1)
N(3)	0.0516(3)	0	0.2236(5)	2.2(2)
N(4A)	0.1360(10)	0.038(2)	0.2926(14)	1.7(5)
N(4B)	0.1393(17)	0	0.292(2)	3(1)
N(5A)	0.2100(15)	0.064(2)	0.3533(18)	5.0(8)
N(5B)	0.2259(12)	0	0.3643(18)	5(1)
N(6)	−0.0970(3)	0	0.4574(4)	2.3(2)
N(7A)	−0.1736(12)	0.041(4)	0.4131(15)	2.2(5)
N(7B)	−0.1840(13)	0	0.4001(17)	2.3(7)
N(8A)	−0.2493(11)	0.078(2)	0.365(2)	5.7(9)
N(8B)	−0.2687(11)	0	0.3416(18)	6(1)
N(9)	−0.1497(3)	0	−0.0467(4)	2.3(2)
N(10)	−0.1622(3)	0	0.0479(4)	1.9(1)
N(11)	−0.1748(3)	0	0.1414(5)	2.8(2)
C(1)	0.0817(3)	0.2518(4)	0.0488(5)	4.2(2)
C(2)	0.0843(3)	0.3717(4)	0.0489(6)	4.3(2)
C(3)	0	0.4355(4)	0	2.5(2)
C(4)	−0.1148(3)	0.2507(4)	0.2739(5)	3.5(2)
C(5)	−0.1188(3)	0.3705(3)	0.2695(5)	3.5(2)
C(6)	−0.0342(3)	0.4353(3)	0.3166(3)	2.1(1)
C(7)	0.0495(3)	0.3722(4)	0.3637(5)	4.0(2)
C(8)	0.0475(3)	0.2518(4)	0.3650(5)	3.9(2)
H(1)	0.1446	0.2011	0.0829	5.1
H(2)	0.1523	0.4071	0.0888	5.2
H(3)	−0.1727	0.2098	0.2447	4.1
H(4)	−0.1792	0.3995	0.2443	4.2
H(5)	0.1002	0.4010	0.3955	4.8
H(6)	0.1070	0.2132	0.3996	4.4

associated bpy. In the mirror plane, sequences Zn(1,2,2,1,2,2,1...) are separated by successive pairs of bridging azide anions, these being of two types. Pairs of Zn(2) are linked in centrosymmetric four-membered ZnN_2Zn rings, pairs of end-on (EO) azides linking the two Zn(2) atoms by way of their terminal nitrogens, N(6), Zn(2)···Zn(2) being 3.335(1) Å and N(6)···N(6) 2.740(7) Å (Table II). Pairs of Zn(2) are linked to either side of Zn(1) (Zn(1)···Zn(2), 4.021(1) Å) by further pairs of azide anions; one links end-on *via* N(3), but the other links in extended mode through its two ends as an EE ligand, N(9) to Zn(1) and N(11) to Zn(2). For the EO ligand Zn(1)–N(3)–Zn(2) is 132.2(2)°, larger than the counterpart value for Zn(2)–N(6)–Zn(2) (101.2(2)°, but comparable with other literature values (*ca* 101°, *e.g.*, Ref. [7])), while the Zn–N–N angles associated with the EE ligand (117.1(1) (N(9)); 107.1(1)° (N(11))) are smaller (*c.f.*, *e.g.*, 121.1°,

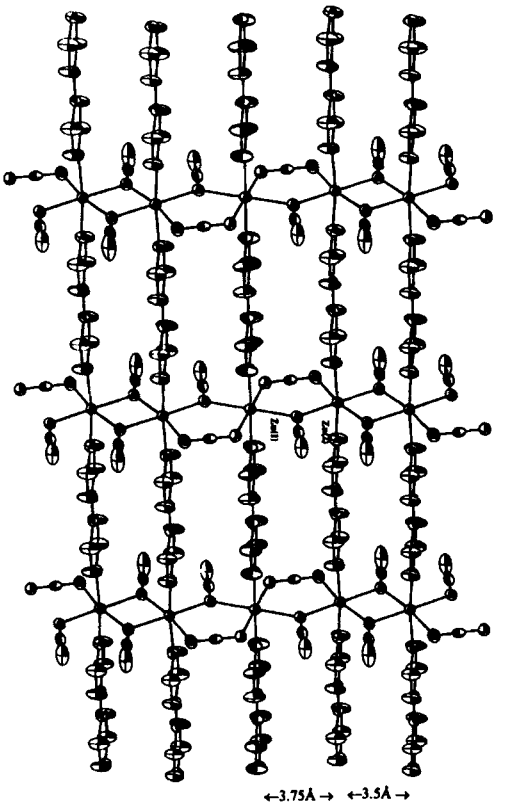

FIGURE 2 Framework of the $[Zn(N_3)_2(4,4'\text{-bipy})]_\infty$ structure shown along the crystallographic *a* direction.

139.4° (Ref. [4(a)])). In consequence of the asymmetry in the Zn(1)···Zn(2) bridges, the array of zinc atoms is not linear, but, rather, form a zigzag chain. Simultaneous EE/EO azide bridges are rare;[8] the present combination of $(EO)_2$ and (EE/EO) forms is novel, possibly consequent here upon the concomitant need for accommodating the parallel stacking of the succession of bpy planes at appropriate spacings, here 3.50 ($(EE)_2$), and 3.75 Å ((EE,EO)), respectively.

Electrical conductivity was measured by a conventional four-probe method at room temperature with a compressed pellet; the electrical conductivity of the compound is $1.1 \times 10^{-9}\,\Omega^{-1}\,cm^{-1}$. The conductivity is high, indicating the unique self-assembly of the structure and a possible large charge interaction of the π–π stacked column.

TABLE II Selected bond lengths (Å) and bond angles (°)

Bond lengths	Zn(1)–N(1)	2.169(4)	Zn(2)–N(6)[c]	2.139(4)
	Zn(1)–N(1)[a]	2.169(4)	Zn(2)–N(2)	2.178(3)
	Zn(1)–N(9)	2.175(4)	Zn(2)–N(2)[a]	2.178(3)
	Zn(1)–N(9)[b]	2.175(4)	Zn(2)–N(6)	2.178(4)
	Zn(1)–N(3)	2.215(4)	Zn(2)–N(3)	2.183(4)
	Zn(1)–N(3)[b]	2.215(4)	Zn(2)–N(11)	2.274(5)
Bond angles	N(1)–Zn(1)–N(1)[a]	180.00	C(1)d–N(1)–Zn(1)	122.2(2)
	N(1)–Zn(1)–N(9)	90.02(1)	C(1)–N(1)–Zn(1)	122.2(2)
	N(1)–Zn(1)–N(9)[b]	89.98(1)	C(8)–N(2)–Zn(2)	120.1(3)
	N(1)–Zn(1)–N(3)	90.02(1)	C(4)–N(2)–Zn(2)	123.7(3)
	N(1)–Zn(1)–N(3)[b]	89.98(1)	N(4B)–N(3)–Zn(2)	116.6(8)
	N(1)a–Zn(1)–N(9)	89.98(1)	N(4B)–N(3)–Zn(1)	111.2(8)
	N(1)a–Zn(1)–N(9)[b]	90.02(1)	N(4A)–N(3)–Zn(2)	113.2(6)
	N(1)a–Zn(1)–N(3)	89.98(1)	N(4A)a–N(3)–Zn(1)	111.5(6)
	N(1)a–Zn(1)–N(3)[b]	90.02(1)	N(4A)a–N(3)–Zn(2)	113.2(6)
	N(9)–Zn(1)–N(9)[b]	180.00	N(4A)–N(3)–Zn(1)	111.5(6)
	N(9)–Zn(1)–N(3)	89.9(2)	Zn(2)–N(3)–Zn(1)	132.2(2)
	N(9)–Zn(1)–N(3)[b]	90.1(2)	N(3)–Zn(1)–N(3)[b]	180.00
	N(9)b–Zn(1)–N(3)	90.1(2)	N(6)c–Zn(2)–N(2)	93.95(8)
	N(9)b–Zn(1)–N(3)[b]	89.9(2)	N(10)–N(9)–Zn(1)	117.1(3)
	N(6)c–Zn(2)–N(2)[a]	93.93(8)	N(2)–Zn(2)–N(11)	86.31(8)
	N(6)c–Zn(2)–N(6)	78.8(2)	N(2)a–Zn(2)–N(6)	91.45(8)
	N(6)c–Zn(2)–N(3)	98.9(2)	N(2)a–Zn(2)–N(3)	88.70(8)
	N(6)c–Zn(2)–N(11)	167.6(2)	N(2)a–Zn(2)–N(11)	86.32(8)
	N(2)–Zn(2)–N(2)[a]	172.0(2)	N(6)–Zn(2)–N(3)	177.7(2)
	N(2)–Zn(2)–N(6)	91.51(8)	N(6)–Zn(2)–N(11)	88.8(2)
	N(2)–Zn(2)–N(3)	88.64(8)	N(3)–Zn(2)–N(11)	93.5(2)

Symmetry operator: (a) $x, -y, z$; (b) $-x, -y, -z$; (c) $-x, -y, 1-z$; (d) $-x, y, -z$; (e) $x, 1-y, z$.

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