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Synthesis and structural characterization of three new 1D and 2D zinc(II) azide polymers with some pyridine and pyrazine derivative ligands

Mohamed A.S. Goher [a], Brigitte Bitschnau [b], Beate Sodin [b], Christian Gspan [b], Franz A. Mautner [b,*]

[a] Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426 Ibrahimia, 21321 Alexandria, Egypt
[b] Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria

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Abstract

Three new polymeric zinc(II) azido complexes, namely [Zn(N_3)$_2$(3-Brpy)]$_n$ (**1**), [Zn(N_3)$_2$(4-Etpy)]$_n$ (**2**) and [Zn_2(N_3)$_4$(2,5-dmpyz)]$_n$ (**3**), where Brpy = bromopyridine, Etpy = ethylpyridine and dmpyz = dimethylpyrazine have been prepared and structurally characterized. The IR spectra of these complexes are measured and discussed. The structures of **1** and **2** are similar and feature one-dimensional zigzag chain of [Zn(N_3)$_2$]$_n$ in which each zinc atom is surrounded by double di-end on (EO) bridging azido ligands forming cyclic Zn_2N_2 units. Furthermore, each zinc atom links a N hetero atom of the pyridine moiety leading to ZnN_5 chromophore. The geometry around the zinc center is best described as distorted trigonal bipyramid. Although complex **3** consists of the 1D chain of [Zn(N_3)$_2$]$_n$ with double di-EO azido bridges around each zinc center with almost planar Zn_2N_2 cyclic units, the pyrazinic moiety behaves as a bidentate bridging *N*,*N*′-ligand that binds the zinc centers across the [Zn_2(N_3)$_2$]$_n$ chains extending the structure to be two-dimensional sheets. The Zn … Zn distances within the Zn_2N_2 units are similar, fall within the range of 3.20–3.26 Å, and the azido ligands are asymmetric and linear within experimental error in all of these three complexes.

Keywords: Azide; Zinc(II); Pyridine and pyrazine derivative complexes; Synthesis; Spectra; Crystal structures

1. Introduction

The azido bridged complexes have attracted intense interest due to the coordination versatility of the azido bridge and the magnetic diversity of the complexes [1]. The azido ligand can link two or more metal ions in various modes; μ-1,1 (end-on, EO), μ-1,3 (end-to-end, EE), μ-1,1,3 and others, and mediate magnetic exchange of different nature and magnitude. These modes may simultaneously exist in the same compound in a variety of alternating sequences [2]. These features in conjunction with the presence of coligands, have led to a lot of 1D and 2D architectures with interesting polymeric topologies and/or magnetic properties [3]. An interesting strategy toward high dimensional topologies is to incorporate a second bridging ligand into the metal azido systems. An increasing number of 2D and sometimes 3D systems have been obtained by this strategy, and the second bridging ligands used thus far have been pyridyl-based ditopic ligands such as pyrazine, 4,4′-bipy and their analogues [4].

Compared to the relatively large number of azido-bridged polymers with Mn(II) [5], Ni(II) [6] and Cu(II) [7] reported in the literature, the Zn(II) polymers are still very rare [8,9]. Zinc is well suited [10–12] as its d^{10} configuration permitting a wide variety of symmetries and coordination numbers and it has drawn special attention for its importance in bio-inorganic chemistry [13,14], in addition

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[*] Corresponding author. Tel.: +43 316 873 8234; fax: +43 316 873 8225.
E-mail address: mautner@ptc.tu-graz.ac.at (F.A. Mautner).

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to the relatively appreciable number of reports concerned with the photoluminescence of some zinc(II) complexes [15,16]. Previously we have shown that $Zn(N_3)_2$ interacts with some pyridine derivatives [17], 4-methylpyrimidine [18], pyridine-, and picoline N-oxides [19]. In the case of pyridine-, and 3-picoline-N-oxide we found that these ligands do not participate in coordination to the zinc atom, but just consolidate the 1D $[Zn(N_3)_2(H_2O)_2]$ chains through hydrogen bonding formation [19] which is not the case for 2-picoline N-oxide acting as monodentate ligand [18]. As an extension of that work we used 3-bromopyridine (3-Brpy), 4-ethylpyridine (4-Etpy) and 2,5-dimethyl pyrazine (dmpyz) to compare the type and topology of the resulting complexes. We isolated 1:1 complexes for the pyridinic ligand and 2:1 in case of dmpyz ligand. This report concerns the synthesis and structural characterization of these three new complexes as elucidated by spectroscopic and crystallographic methods.

2. Experimental

2.1. Materials and instrumentation

Elemental analyses were carried out using a Perkin-Elmer analyzer and infrared spectra were recorded on a Perkin-Elmer FTIR Series 1600 spectrophotometer as KBr pellets. Aminopyrazine has been purchased from Aldrich Company, other chemicals were of analytical grade quality and used without further purification. Aqueous hydrazoic acid was obtained with a modified Kipp's generator by decomposition of NaN_3 in H_2SO_4/H_2O (1:3, v:v) and subsequent transfer of HN_3 into H_2O with aid of an inert gas stream [5c,20].

Caution: Azide compounds and hydrazoic acid (HN_3) are potentially explosive! Only a small amount of material should be prepared and handled with care.

2.2. Synthesis

2.2.1. $[Zn(N_3)_2(3\text{-bromopyridine})]_n$ (**1**)

Complex **1** was prepared by mixing 3-bromopyridine (0.06 g, 0.4 mmol) with an aqueous solution of $Zn(N_3)_2$ (22 mL, 8.9 mmol Zn) saturated with hydrazoic acid. The mixture was heated to 70 °C to obtain a clear solution. Upon slow cooling transparent crystals of the complex were deposited after 5 days at room temperature. Yield: 0.074 g, 60%. Analysis: found: C, 19.3; H, 1.2; N, 32.1; Zn, 21.5%. Calculated for $C_5H_4BrN_7Zn$: C, 19.5; H, 1.3; N, 31.9; Zn, 21.3. IR, KBr (cm^{-1}): (v very, s strong, m medium, w weak, br broad): 3573 br, 3387 vw, 3062 vw, 2160 m, 2086 vs, 1585 w, 1465 w, 1415 w, 1343 w, 1295 w, 1190 w, 1122 w, 1097 w, 1028w, 794 w, 693 m, 664 w, 634 w, 408 w.

2.2.2. $[Zn(N_3)_2(4\text{-Ethylpyridine})]_n$ (**2**)

Complex **2** was prepared in a similar procedure as complex **1**. 4-Ethylpyridine (0.85 g, 7.9 mmol) was mixed with an aqueous solution of $Zn(N_3)_2$ (30 mL, 26.6 mmol Zn). The mixture was heated to 65 °C to obtain a clear solution. Colorless transparent crystals of complex **2** were deposited after 1 day at 37 °C. Yield: 1.58 g, 78%. Analysis: found: C, 32.9; H, 3.6; N, 38.8; Zn, 25.2%. Calculated for $C_7H_9N_7Zn$: Calc.: C, 32.8; H, 3.5; N, 38.2; Zn, 25.5. IR, KBr (cm^{-1}): 3402 vw, 3351 w, 2980 w, 2914 w, 2890 w, 2625 w, 2571 w, 2080 vs, 1618 s, 1557 w, 1503 w, 1458 w, 1433 m, 1345 m, 1288 s, 1204 w, 1066 m, 1031 m, 835 m, 788 w, 664 m, 601 w, 576 w, 497 w, 389 w.

2.2.3. $[Zn_2(N_3)_4\,(2,5\text{-dimethylpyrazine})]_n$ (**3**)

Complex **3** was prepared in a similar procedure as complex **1**. 2,5-Dimethylpyrazine (0.52 g, 4.8 mmol) was mixed with an aqueous solution of $Zn(N_3)_2$ (10 mL, 8.9 mmol Zn). The mixture was heated to 80 °C to obtain a clear solution. Colorless transparent crystals of complex **3** were deposited after 1 day at room temperature. Yield: 1.22 g, 67%. Analysis: found: C, 17.5; H, 1.9; N, 48.4; Zn, 32.2%. Calculated for $C_6H_8N_{14}Zn_2$: Calc.: C, 17.7; H, 2.0; N, 48.2; Zn, 32.1. IR, KBr (cm^{-1}): 3572 br, 3361 w, 3129 w, 3049 w, 2630 w, 2576 w, 2140 s, 2091 vs, 1500 m, 1445 w, 1345 m, 1291 s, 1189 w, 1159 m, 1074 m, 1035 w, 972 w, 900 w, 667 m, 596 w, 529 w, 444 m.

2.3. X-ray crystallography

Single crystal X-ray data for complexes **1** and **2** were measured at 90(2) K on a modified STOE four circle diffractometer, and for **3** at 100(2) K on a Bruker-AXS SMART APEX CCD diffractometer, using graphite crystal-monochromatized Mo-Kα; radiation ($\lambda = 0.7107$ Å). The intensities were corrected for Lorentz-polarisation effects, intensity decay and for absorption. Crystallographic data and processing parameters are given in Table 1. The structures were solved by direct methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles. Geometrical restraints were applied for all hydrogen atoms and also for the twofold disordered 4-ethylpyridine molecule of **2**. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The programs DIFABS, SADABS [21] and SHELXTL/PC program package [22] were used for computations. Selected bond distances and bond angles are given in Tables 2–4, for complexes **1**–**3**, respectively.

3. Results and discussion

3.1. Structures

3.1.1. $[Zn(N_3)_2(3\text{-Brpy})]$ (**1**)

Fig. 1a illustrates the principle structural features of complex **1** along with a labeling scheme, selected bond

Table 1
Crystallographic data and processing parameters

Compound	**1**	**2**	**3**
Empirical formula	$C_5H_4BrN_7Zn$	$C_7H_9N_7Zn$	$C_3H_4N_7Zn$
Formula mass	307.44	256.60	203.52
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$I2/a$	$P2_1/c$
a (Å)	6.038(2)	6.109(3)	7.4356(15)
b (Å)	21.255(7)	17.722(5)	15.585(3)
c (Å)	7.528(4)	9.544(2)	6.1639(12)
α (°)	90	90	90
β (°)	98.37(3)	101.65(2)	102.11(3)
γ (°)	90	90	90
V (Å^3)	955.8(7)	1012.0(6)	698.4(2)
Z	4	4	4
μ (MoKα) (mm^{-1})	6.720	2.405	3.456
D_{calc} (Mg/m^3)	2.136	1.684	1.936
Crystal size (mm)	0.24 × 0.12 × 0.10	0.30 × 0.25 × 0.20	0.35 × 0.28 × 0.20
θ Range (°)	2.90–26.99	3.59–26.98	2.61–26.37
Reflections collected	2669	1367	5322
Independ. refl./R_{int}	2086/0.0419	1105/0.0321	1421/0.0448
Parameters	127	106	101
Goodness of Fit on F^2	1.063	1.291	1.117
R_1/wR_2 [$I > 2\sigma(I)$]	0.0367/0.0859	0.0544/0.1458	0.0450/0.1167
R_1/wR_2 (all data)	0.0447/0.0927	0.0557/0.1465	0.0528/ 0.1336
Residual extrema (e/Å^3)	0.721/−0.702	0.667/−1.835	1.125/−1.100

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Zn(1)...Zn(1A)	3.200(1)	Zn(1)...Zn(1B)	3.262(1)
Zn(1)–N(21)	2.007(3)	Zn(1)–N(11)	2.007(4)
Zn(1)–N(1)	2.033(3)	Zn(1)–N(11A)	2.132(3)
Zn(1)–N(21B)	2.250(3)	N(11)–N(12)	1.206(5)
N(12)–N(13)	1.151(5)	N(21)–N(22)	1.209(5)
N(22)–N(23)	1.139(5)	C(2)–Br(1)	1.885(4)
Zn(1A)...Zn(1)...Zn(1B)	138.26(3)	N(21)–Zn(1)–N(11)	126.9(2)
N(21)–Zn(1)–N(1)	112.90(14)	N(11)–Zn(1)–N(1)	119.48(14)
N(21)–Zn(1)–N(11A)	98.05(13)	N(11)–Zn(1)–N(11A)	78.7(2)
N(1)–Zn(1)–N(11A)	102.80(14)	N(21)–Zn(1)–N(21B)	80.12(14)
N(11)–Zn(1)–N(21B)	91.41(13)	N(1)–Zn(1)–N(21B)	90.36(13)
N(11A)–Zn(1)–N(21B)	166.25(13)	N(12)–N(11)–Zn(1)	125.6(3)
N(12)–N(11)–Zn(1A)	133.1(3)	Zn(1)–N(11)–Zn(1A)	101.3(2)
N(13)–N(12)–N(11)	179.8(4)	N(22)–N(21)–Zn(1)	121.5(3)
N(22)–N(21)–Zn(1B)	122.5(3)	Zn(1)–N(21)–Zn(1B)	99.88(14)
N(23)–N(22)–N(21)	178.2(4)		

Symmetry codes: (A) $-x, -y+1, -z$; (B) $-x+1, -y+1, -z$.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Zn(1)–N(11)	2.008(5)	Zn(1)–N(11A)	2.008(5)
Zn(1)–N(1)	2.025(8)	Zn(1)–N(1A)	2.025(8)
Zn(1)–N(11B)	2.203(5)	Zn(1)–N(11C)	2.203(5)
N(11)–N(12)	1.214(7)	N(12)–N(13)	1.134(7)
Zn(1)...Zn(1B)	3.262(2)		
N(11)–Zn(1)–N(11A)	119.8(3)	N(11)–Zn(1)–N(1)	116.0(5)
N(11A)–Zn(1)–N(1)	124.3(5)	N(11)–Zn(1)–N(1A)	124.3(5)
N(11A)–Zn(1)–N(1A)	116.0(5)	N(1)–Zn(1)–N(1A)	8.3(10)
N(11)–Zn(1)–N(11B)	78.5(2)	N(11A)–Zn(1)–N(11B)	97.8(2)
N(1)–Zn(1)–N(11B)	93.0(4)	N(1A)–Zn(1)–N(11B)	94.2(4)
N(11)–Zn(1)–N(11C)	97.8(2)	N(11A)–Zn(1)–N(11C)	78.5(2)
N(1)–Zn(1)–N(11C)	94.2(4)	N(1A)–Zn(1)–N(11C)	93.0(4)
N(11B)–Zn(1)–N(11C)	172.8(3)	N(12)–N(11)–Zn(1)	123.1(4)
N(12)–N(11)–Zn(1B)	123.3(4)	Zn(1)–N(11)–Zn(1B)	101.5(2)
N(13)–N(12)–N(11)	178.7(7)	Zn(1B)...Zn(1)...Zn(1C)	138.88(6)

Symmetry codes: (A) $-x+1/2, y, -z$; (B) $-x, -y, -z$; (C) $x+1/2, -y, z$.

distances and bond angles are listed in Table 2. The coordination of the zinc(II) atom by 3-Brpy and azido ligands may be described as distorted trigonal bipyramid ($\tau = 0.66$) with N(11A) and N(21B) at the apical positions. In the asymmetric unit, μ-1,1 azido groups [N(11)–N(12)–N(13) and N(11A)–N(12A)–N(13A)] lying on the same crystallographic diad bridge a pair of zinc atoms [Zn(1) and Zn(1A)] related by an inversion center forming a planar Zn_2N_2 cyclic ring, whereas μ-1,1 azide ligands [N(21)–N(22)–N(23) and N(21B)–N(22B)–N(23B)] link Zn(1) and Zn(1B) atoms forming another Zn_2N_2 ring, giving rise to zigzag chains of zinc polyhedra along the a-axis of the unit cell (Fig. 1b). The shortest and longest metal–ligand bonds are Zn–N(11) = 2.007(3) and Zn–N(23) = 2.252(3) Å, respectively, while the other three are virtually equal to 2.007(3)–2.132(3) Å (Table 2) and compare well with corresponding distances in other zinc(II) azide complexes of pyridine derivative ligands [17]. Both μ-1,1 azido ligands are asymmetric [N(11)–N(12) = 1.206(5), N(12)–N(13) = 1.151(5) Å and N(21)–N(22) = 1.209(5), N(22)–N(23) = 1.139(5) Å] and linear within experimental error [N–N–N angles of 178.2(4) and 179.8(4)°]. The Zn...Zn distances within the cyclic four-membered Zn_2N_2 rings are 3.200(1) and 3.262(1) Å.

3.1.2. $[Zn(N_3)_2(4\text{-}Etpy)]_n$ (2)

The structural features of complex **2** are shown in Fig. 2a, and bond parameters are collected in Table 3. The structure of complex **2** features five coordinate zinc

Table 4
Selected bond lengths (Å) and angles (°) for **3**

Zn(1)…Zn(1A)	3.256(1)	Zn(1)…Zn(1B)	6.962(1)
Zn(1)–N(11A)	2.028(3)	Zn(1)–N(21)	2.036(3)
Zn(1)–N(1)	2.104(3)	Zn(1)–N(11)	2.142(3)
Zn(1)–N(21A)	2.179(3)	N(11)–N(12)	1.218(5)
N(12)–N(13)	1.137(5)	N(21)–N(22)	1.210(5)
N(22)–N(23)	1.147(5)		
Zn(1A)…Zn(1)…Zn(1B)	142.39(3)	N(11A)–Zn(1)–N(21)	124.81(14)
N(11A)–Zn(1)–N(1)	128.29(12)	N(21)–Zn(1)–N(1)	106.45(12)
N(11A)–Zn(1)–N(11)	100.47(14)	N(21)–Zn(1)–N(11)	78.45(13)
N(1)–Zn(1)–N(11)	95.45(11)	N(11A)–Zn(1)–N(21A)	77.76(13)
N(21)–Zn(1)–N(21A)	97.88(13)	N(1)–Zn(1)–N(21A)	89.97(11)
N(11)–Zn(1)–N(21A)	174.13(12)	N(12)–N(11)–Zn(1C)	125.0(3)
N(12)–N(11)–Zn(1)	131.0(3)	Zn(1C)–N(11)–Zn(1)	102.64(14)
N(13)–N(12)–N(11)	179.0(4)	N(22)–N(21)–Zn(1)	127.8(3)
N(22)–N(21)–Zn(1C)	128.3(3)	Zn(1)–N(21)–Zn(1C)	101.09(14)
N(23)–N(22)–N(21)	178.7(4)		

Symmetry codes: (A) $x, -y+3/2, z+1/2$; (B) $-x, -y+1, -z$; (C) $x, -y+3/2, z-1/2$.

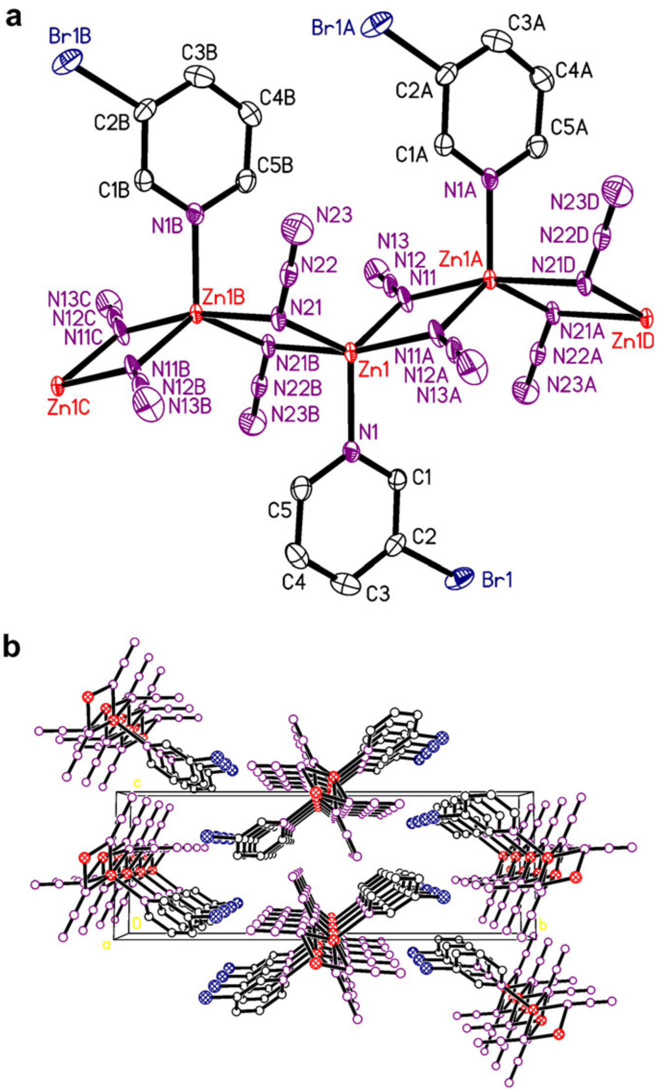

Fig. 1. (a) Perspective view with atom labeling scheme of (**1**). Symmetry codes according Table 2. (b) Packing plot of (**1**) viewed along the *a*-axis of the unit cell.

atoms, each zinc is surrounded by two di-EO (end-on) azide bridges; N(11), N(11A), N(11B), N(11C) [Zn–N = 2.008(5) and 2.203(5) Å], and the fifth position is occupied by N atom of 4-Etpy ligand [Zn–N = 2.025(8) Å]. The 1D chain of polyhedra (Fig. 2b) is extended along the *a*-axis of the unit cell. The Zn…Zn distances within the four-member Zn_2N_2 units are 3.262(2) Å. As in complex **1**, the μ-1,1 azido groups are asymmetric and almost linear within experimental error.

3.1.3. [$Zn_2(N_3)_4$ (2,5-dmpyz)]$_n$ (**3**)

Crystal structure analysis has revealed that the ratio of $Zn(N_3)_2$ to 2,5-dmpyz is exactly 2:1 as inferred from the elemental analysis. A view of the asymmetric unit along with a labeling scheme is given in Fig. 3a, and selected bond lengths and bond angles are given in Table 4. The structure consists of a chain of $Zn(N_3)_2$ in which each zinc atom binds two di-EO bridging azides and extended along the *c*-axis of the unit cell. The fifth position is occupied by a nitrogen atom from 2,5-dmpyz ligand forming ZnN_5 chromophore having distorted trigonal bipyramid (TBP) geometry (τ = 0.76) with N(11), and N(21A) at the axial positions. The Zn–N(N_3) distances are variable from 2.026(3) to 2.142(3) Å, which are more or less similar to corresponding values given for complexes **1** and **2**. Each

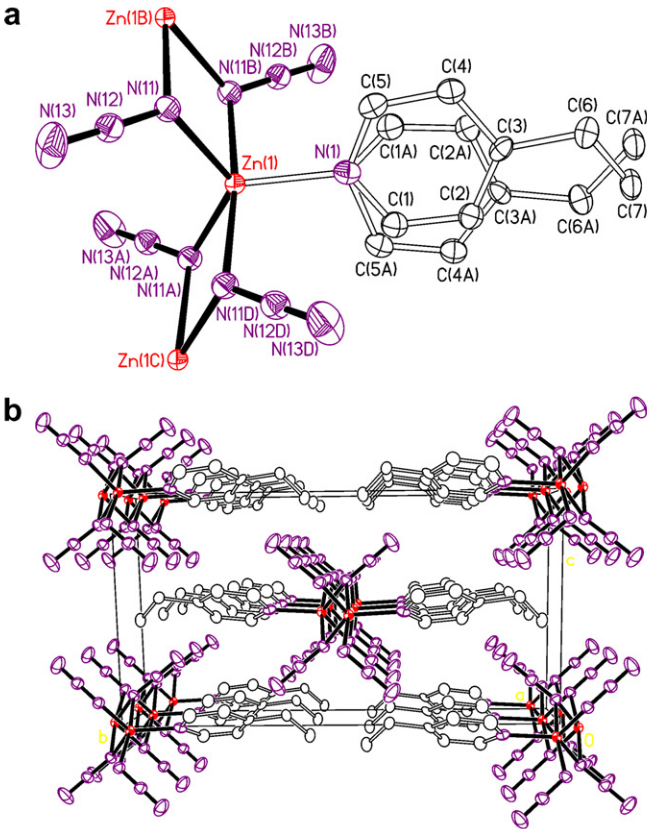

Fig. 2. (a) Perspective view with atom labeling scheme of (**2**). Symmetry codes according Table 3. (b) Packing plot of (**2**) viewed along the *a*-axis of the unit cell.

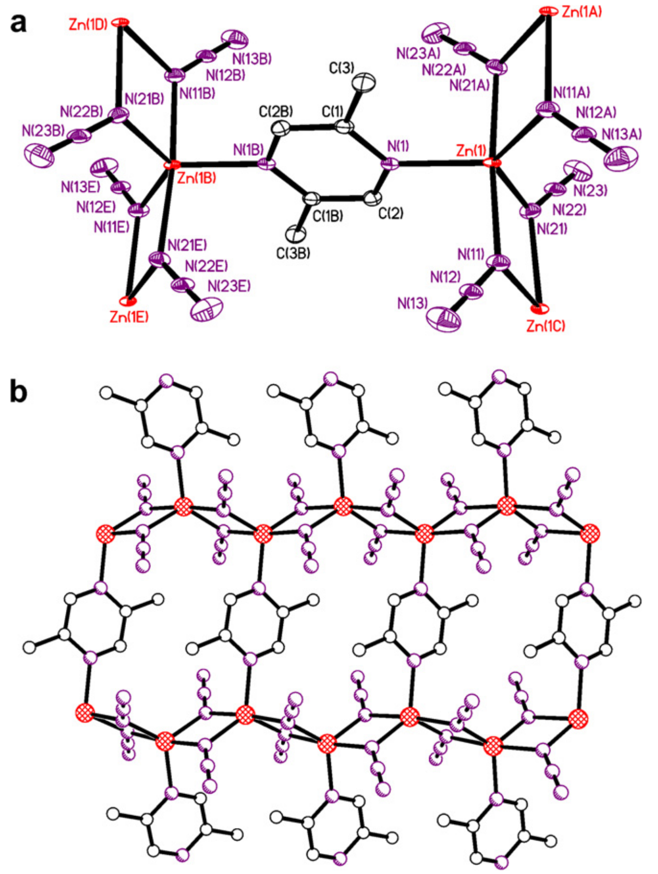

Fig. 3. (a) Perspective view with atom labeling scheme of (**3**). Symmetry codes according Table 4. (b) 2D arrangement of (**3**). The sheets are extended along the *b*- and *c*-axes of the unit cell.

of the dmpyz ligands binds another zinc atom in adjacent $Zn(N_3)_2$ chains via its second nitrogen extending the structure along the *b*-axis to form 2D sheets (Fig. 3b). The pyrazine ligand has a Zn–N(pyz) bond distance of 2.104(3) Å, which is a little longer than corresponding values found in complexes **1** and **2** with monodentate pyridine ligands, whereas the Zn…Zn distance within the Zn_2N_2 units of 3.256(1) Å, is very close to those found in complexes **1** and **2**.

3.2. Discussion

The reaction between $Zn(N_3)_2$ and 3-Brpy, 4-Etpy and 2,5-dmpyz afforded 1:1 zinc(II) azide to ligand in case of the first two pyridine derivatives and 2:1 in case of the pyrazinic ligand. Maybe this is related to the ability of the third ligand to behave as a bridging bidentate. Although the structures of complexes **1** and **2** are similar: both crystallize in monoclinic, features 1D chains consisting of two di-EO azido bridges around each zinc center which is further connected to the monodentate pyridine derivative ligand having therefore ZnN_5 chromophore, there are subtle differences. Crystals of complex **1** are monoclinic, space group $P2_1/c$, whereas the space group of complex **2** is I2/a. The Zn(1)–N(11)–N(12) and Zn(1B)–N(11)–N(12) angles of 123.1(4) and 123.3(4)°, respectively, in complex **1**, are within the 120° angle of sp^2 hybridized nitrogen atom of the azido ligands, whereas the corresponding angles Zn(1)–N(11)–N(12) and Zn(1A)–N(11)–N(12) in complex **2** of 125.6(3) and 133.1(3)° are greater than the 120° angle. Both complexes however, differ from the structure of complex **3**, with the 2D sheet structure and bridging bidentate *N*,*N*′-dmpyz ligand. The structure of complex **3** differs also from that of $[Zn_3(N_3)_6(ampyz)_2]_n$ **4** (ampyz = aminopyrazine), also having 2D sheet structure [23]. Complex **4** contains two crystallographically different zinc centers: Zn(1) is octahedrally coordinated by two di-EO azido bridges and two trans ampyz ligands giving ZnN_6 chromophore, whereas Zn(2) is five coordinated by two di-EO bridging azides and one ampyz forming ZnN_5 chromophore, and each ampyz links another zinc center. Complex **4**, thus having chains of alternate ZnN_6/ZnN_5.

It is noteworthy at this point to compare complexes **1** and **2** with known zinc(II) azide complexes of the same formula $[Zn(N_3)_2L]_n$ for L = 2-picoline [17c], 3-picoline [17b], 4-picoline [17d], lutidines [17a] and 4-methylpyrimidine [18]. All these structures are very similar adopting ZnN_5 geometries with distorted trigonal bipyramids. The asymmetric end-on (μ-1,1) azide bridges form 1D chains with common edges, with one equatorial Zn–N bond [from 1.99 to 2.05 Å, mean value 2.02 Å] and one longer axial Zn–N bond [range from 2.11 to 2.28 Å, mean 2.22 Å], respectively. Due to low steric hindrance of the azido bridges the difference of axial and equatorial Zn–N bonds of 0.20 Å is in good agreement with theoretical calculation done for d^{10} systems by Gillespie [24]. In all the above eight complexes the Zn–N(pyridine) bond range is 1.99–2.06 Å (mean value 2.02 Å), the Zn…Zn distances range from 3.03 to 3.31 Å, and Zn…Zn…Zn angles from 134° to 140°. Metal azide complexes similar to **1** and **2**, featuring five coordinate metal centers, two di-EO azido bridges forming zigzag chains, and distorted trigonal bipyramid or distorted square pyramid have been reported previously in numerous structures of copper(II) azido complexes of pyridine derivatives, e.g. $[Cu(N_3)_2(3\text{-picoline})]_n$ [25], $[Cu(N_3)_2(2\text{-chloropyridine})]_n$ [26] and $[Cu(N_3)_2(2,5\text{-dimethyl pyridine})]_n$ [27].

The IR spectrum of complex **1**, shows a very strong band at 2086 cm^{-1}, and another strong band at 2042 cm^{-1}, in addition to two medium to strong bands at 1343 and 1286 cm^{-1}, due to $\nu_{as}(N_3)$ and $\nu_s(N_3)$ vibration modes. The high frequency vibrations are consistent with the crystal structure determination that the complex contains two μ-1,1 azido bridges with different degrees of asymmetry [$\Delta d = 0.070$ Å for one, and 0.055 Å for the other (Δd is the difference between the N–N distances within the azide group)], and the 1350–1280 cm^{-1} bands confirm the asymmetric nature of the azides. Complex **2** with two μ-1,1 azido bridges having the same degree of asymmetry [$\Delta d = 0.080$ Å] only one very strong band associated with $\nu_{as}(N_3)$ vibration mode appears at 2080 cm^{-1}, in addition to two strong bands at 1345 and 1288 cm^{-1}

due to $\nu_s(N_3)$. The IR spectrum of complex **3**, exhibits a very strong band at 2091 cm^{-1} related to $\nu_{as}(N_3)$, although the structure contains two μ-1,1 bridging azides of different degrees of asymmetry [$\Delta d = 0.081$ Å for one and 0.063 Å for the other]. The appearance of two strong bands at 1345 and 1291 cm^{-1}, however is a strong evidence of the asymmetric nature of the azido groups in this complex. Although the positions of the $\nu_{as}(N_3)$ mode for complexes **1** and **2** are consistent with the relationship pointed out previously that the larger the difference between the two N–N distances within the azido group (Δd), the higher is the energy of $\nu_{as}(N_3)$ [28], the position of the $\nu_{as}(N_3)$ for complex **3** shows no consistency.

4. Conclusion

We isolated three zinc(II) azido polymers with 3-bromopyridine, 4-ethylpyridine and 2,5-dimethylpyrazine, with 1:1 molar ratio for pyridine derivative ligands and 2:1 ratio in case of the pyrazinic ligand, and studied their spectra and crystal structures. As the pyridine ligands contain only one coordination site; the hetero nitrogen, the structures of both 1:1 complexes confined to 1D chain. As the pyrazine derivative ligand can behave as a bidentate bridge, allows the structure of complex **3** to extend to be 2D sheets. The IR spectral results confirm the asymmetric nature of azido groups in the three complexes.

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Appendix A. Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers: CCDC-657313–CCDC-657315 for **1**–**3**, respectively.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.10.030.

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