Ladders, rings and cubes as structural motifs in three new zinc(II) azide complexes: Synthesis, spectral and structural characterization

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Abstract

Three new zinc(II) azide complexes, namely $\{[Zn_2(N_3)_4(py\text{-}tetrazole)_2](py\text{-}tetrazole)\}_n$ (**1**), $\{[Zn_2(N_3)_4(3\text{-}OHpy)] \cdot 2H_2O\}_n$ (**2**) and $[Zn(N_3)_2(pym)]_n$ (**3**), where py-tetrazole = tetrazolo[1,5-*a*]pyridine, 3-OHpy = 3-hydroxypyridine and pym = pyrimidine, have been synthesized by the hydrothermal methods and structurally characterized. The ligand py-tetrazole was obtained through the interaction of 2-chloropyridine with the azide ion under hydrothermal condition. The structure of **1** consists of a ladder-like arrangement of 1D double chain zinc(II) azide. In the coordination chain, each zinc atom binds di-EO azide bridges connecting another zinc atom in opposite chain, and two EO bridges, one on each side, and the fifth position is occupied by a N atom of py-tetrazole ligand. The structure of **2** features 2D sheets composed of tetranuclear zinc(II) ring and octanuclear zinc(II) ring interconnected by EO azide bridges. The 2D carrying into 3D supramolecular network by the help of several hydrogen bonding interactions. The 3-OHpy molecule acts in the tautomeric keto-form as *O,O*-bidentate bridging ligand. Complex **3** features distorted octahedral geometry around each zinc center, *N,N'*-bidentate pyrimidine ligand and EE azido bridges leading to 3D network structure. The IR spectra are measured and discussed. Complex **2** only exhibits photoluminescence properties whereas the other two complexes do not luminesce at room temperature.
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1. Introduction

The use of the principles of crystal engineering in the preparation of supramolecular coordination polymers analogous to important material such as zeolites has received a considerable interest during the last decade [1,2]. The crystal engineering of coordination polymers is usually achieved by using bi-, or multi-dentate ligands to connect the metal centers. Two types of coordinating ligands: (i) neutral organic e.g. pyrazine, 4,4′-bipyridine [3–5], etc., and (ii) anionic, e.g. azide, thiocyanate [6–8], polyaromatic acid anions [9], etc., are used to synthesize interesting one-, two-, or three-dimensional polymers with variable cavities or channels [4]. Among the anionic ligands, the azide ion is a versatile ligand and exhibits a variety of bridging abilities including bi-dentate end-on (μ-1,1-EO) or end-to-end (μ-1,3-EE) [10–12] bridging fashion, and tri-μ-1,1,3 mode [13] and others [14]. These modes can exist simultaneously in the same compound affording a variety of nuclearities and interesting physical properties [10–14]. In this context, zinc is well suited [15] due to its d^{10} configuration which permits a wide variety of symmetries and coordination numbers. Also the photoluminescence of zinc(II) complexes has received a considerable interest in the last few years [16,17]. To explore the combination effects of potentially bi-dentate organic ligands (Scheme 1) and anionic azide

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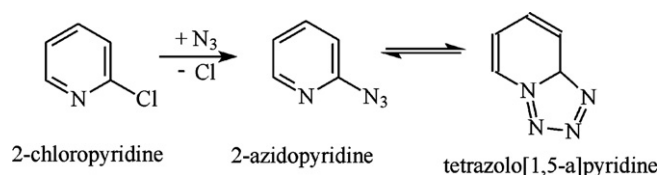
Scheme 1.

we synthesized coordination polymers of Zn(II) containing these ligands. The ligand (L1) in the scheme in fact was prepared through the reaction between 2-chloropyridine and azide ion, forming tetrazolo[1,5-a]pyridine (abbreviated as py-tetrazole). This ligand is a potentially multi-dentate ligand, however, it acts in the synthesized complex $[Zn_2(N_3)_4(py\text{-}tetrazolate)_2](py\text{-}tetrazole)$ (1) as a monodentate and links zinc center not through the pyridinic nitrogen but through a nitrogen atom of the other three tetrazole nitrogens. This complex crystallizes with uncoordinated py-tetrazole molecule. The second ligand L2 in the scheme: 3-hydroxypyridine (3-OHpy), behaves as *O,O*-bridging, i.e. in the tautomeric keto-form (pyridone) in the prepared zinc(II) complex, $[Zn_2(N_3)_4(3\text{-}OHpy)] \cdot 2H_2O$ (2) which crystallizes with two lattice water molecules. L3 is pyrimidine (pym) which is potentially bidentate and has the ability to bridge metal centers, afforded $[Zn(N_3)_2(pym)]$ (3). The structural motifs of these complexes are variable from ladder (1D), to rings (2D) and cubes (3D). Complexes 1 and 2 are unprecedented in all known metal azide complexes. These three new complexes are studied by spectroscopic methods and X-ray crystal diffraction. The room temperature photoluminescence of complex 2 is measured. The results of this study are reported here.

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 [18]. Luminescence spectra were recorded on a Yobin Yvon SPEX Fluoromax 2 instrument. Starting ligands have been purchased from Aldrich Company, other chemicals were of analytical grade quality and used without further purification. Aqueous hydrazoic acid is 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. Stock solutions of aqueous ZnN_6 (0.89 mmol Zn/mL H_2O) are obtained in a similar manner by the reaction of HN_3 with a suspension of basic zinc carbonate (0.10 g/mL) H_2O [19].

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. $\{[Zn_2(N_3)_4(py\text{-}tetrazole)_2](py\text{-}tetrazole)\}_n$ (1)

Complex 1 was prepared by mixing an aqueous solution of ZnN_6 saturated with hydrazoic acid (10 mL, 8.9 mmol Zn) with 2-chloropyridine (0.50 g, 4.4 mmol) in MeOH (10 mL). The mixture was heated to 95 °C for 30 min with subsequent step-wise cooling to 4 °C. Needle-shaped colorless crystals of the complex were deposited after approx.12 weeks. Yield: approx. 55%. *Anal*. Calc. for $C_{15}H_{12}N_{24}Zn_2$:

Table 1
Crystallographic data and processing parameters

Compound	1	2	3
Empirical formula	$C_{15}H_{12}N_{24}Zn_2$	$C_5H_9N_{13}O_3Zn_2$	$C_4H_4N_8Zn$
Formula mass	659.27	430.03	229.54
System	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$I2/m$
a (Å)	12.909(3)	11.635(2)	7.508(2)
b (Å)	6.740(2)	10.743(2)	12.083(3)
c (Å)	28.312(9)	11.999(2)	8.500(3)
α (°)	90	90	90
β (°)	94.43(2)	104.40(3)	91.67(2)
γ (°)	90	90	90
V (Å^3)	2456.0(12)	1452.7(5)	770.8(4)
Z	4	4	4
T (K)	293(2)	100(2)	99(2)
μ (Mo Kα) (mm^{-1})	2.015	3.341	3.148
D_{calc} (Mg/m^3)	1.783	1.966	1.978
Crystal size (mm)	$0.35 \times 0.22 \times 0.16$	$0.38 \times 0.30 \times 0.20$	$0.30 \times 0.20 \times 0.12$
θ Range (°)	3.11–26.00	1.81–25.49	2.93–29.99
Reflections collected	5586	10251	1494
Independent reflections (R_{int})	4786(0.0328)	2700(0.1071)	1178(0.0283)
Parameters	370	220	65
Goodness-of-fit on F^2	1.122	1.097	1.255
R_1/wR_2	0.0407/0.0999	0.0608/0.1433	0.0361/0.0982
Residual extrema (e Å^3)	0.509, −0.524	1.189, −1.089	0.499, −0.668

C, 27.3; H, 1.8; N, 51.0. Found: C, 27.1; H, 1.9; N, 50.8%. IR, KBr (cm^{-1}): (v, very; s, strong; m, medium; w, weak; br, broad): 3134 w, 3107 w, 3086 w, 3037 w, 2118 s, 2098 vs, 1630 m, 1492 m, 1431 w, 1302 w, 1285 m, 1266 w, 1139 m, 1093 m, 1021 w, 771 m, 749 m, 691 w, 674 w, 599 w, 556 w, 428 w.

2.2.2. {[Zn$_2$(N$_3$)$_4$(3-OHpy)] · 2H$_2$O}$_n$ (2)

This complex was prepared by dissolving 3-hydroxypyridine (0.358 g, 3.76 mmol) in an aqueous solution of ZnN$_6$ saturated with hydrazoic acid (10 mL, 8.9 mmol Zn). The clear solution was stored at 4 °C to separate colorless and transparent crystals of the complex after 7 days. Yield: approx. 55%. *Anal.* Calc. for C$_5$H$_9$N$_{13}$O$_3$Zn$_2$: C, 14.0; H, 2.1; N, 42.3. Found: C, 14.2; H, 1.9; N, 42.6%. IR, KBr (cm^{-1}): 3599 mbr, 3468 br, 3115 w, 2121 vs, 2091 vs, 1603 m, 1549 m, 1471 m, 1357 m, 1305 m, 1260 m, 1179 vw, 1109 vw, 1046 vw, 1002 vw, 853 m, 805 m, 697 w, 674 m, 619 w, 580 w, 525 w.

2.2.3. [Zn(N$_3$)$_2$(pym)]$_n$ (3)

This complex was prepared by mixing an aqueous solution of ZnN$_6$ saturated with hydrazoic acid (15 mL, 8.9 mmol Zn) with pyrimidine (83.9 mg, 1.27 mmol). The mixture was heated to 80 °C to obtain a clear solution. Colorless crystals of the complex were deposited after 2 days at room temperature. Yield: approx. 80%. *Anal.* Calc. for C$_4$H$_4$N$_8$Zn: C, 20.9; H, 1.8; N, 48.8. Found: C, 48.5; H, 1.7; N, 20.8%. IR, KBr (cm^{-1}): 3422 w, 3393 w, 3105 w, 3087 w, 2078 vs, 1594 s, 1563 m, 1463 m, 1420 m, 1286 w, 1219 w, 1175 m, 1136 w, 1075 m, 1021w, 957 w, 819 m, 704 s, 685 m, 649 m, 656 s 616 m.

2.3. X-ray crystallography

Single crystal X-ray data for complexes **1** and **3** were measured on a modified STOE four circle diffractometer, and for **2** 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 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 by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The programs DIFABS, SADABS and SHELXTL/PC program package [20] were used for computations. Selected bond distances and bond angles are given in Tables 2, 4 and 6, for complexes **1**–**3**, respectively. Hydrogen bonds of complex **2** are summarized in Table 5.

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

Zn(1)–N(41)	2.047(3)	Zn(1)–N(31)	2.063(3)
Zn(1)–N(21)	2.085(3)	Zn(1)–N(11)	2.087(3)
Zn(1)–N(1)	2.252(3)	Zn(2)–N(31A)	2.038(3)
Zn(2)–N(41B)	2.050(3)	Zn(2)–N(21)	2.059(3)
Zn(2)–N(11)	2.120(3)	Zn(2)–N(5)	2.253(3)
N(11)–N(12)	1.208(4)	N(12)–N(13)	1.139(4)
N(21)–N(22)	1.206(4)	N(22)–N(23)	1.149(4)
N(31)–N(32)	1.226(4)	N(32)–N(33)	1.131(4)
N(41)–N(42)	1.224(4)	N(42)–N(43)	1.140(4)
N(1)–C(5)	1.337(5)	N(1)–N(2)	1.347(4)
N(2)–N(3)	1.297(4)	N(3)–N(4)	1.358(5)
N(4)–C(5)	1.353(5)	N(4)–C(1)	1.375(5)
N(5)–C(10)	1.337(5)	N(5)–N(6)	1.356(4)
N(6)–N(7)	1.297(5)	N(7)–N(8)	1.367(5)
N(8)–C(10)	1.345(5)	N(8)–C(6)	1.370(5)
N(18)–C(17)	1.311(6)	N(18)–N(19)	1.387(10)
C(17)–N(16)	1.337(6)	C(21)–N(16)	1.398(6)
N(16)–N(20)	1.359(7)	N(20)–N(19)	1.211(9)
Zn(1)···Zn(2)	3.2256(11)	Zn(1)···Zn(2B)	3.5929(13)
Zn(1)···Zn(2A)	3.6003(13)		
N(41)–Zn(1)–N(31)	115.20(12)	N(41)–Zn(1)–N(21)	112.70(13)
N(31)–Zn(1)–N(21)	132.04(13)	N(41)–Zn(1)–N(11)	98.67(12)
N(31)–Zn(1)–N(11)	96.60(12)	N(21)–Zn(1)–N(11)	78.30(11)
N(41)–Zn(1)–N(1)	94.60(11)	N(31)–Zn(1)–N(1)	88.04(12)
N(21)–Zn(1)–N(1)	86.00(11)	N(11)–Zn(1)–N(1)	162.43(12)
N(31A)–Zn(2)–N(41B)	117.56(12)	N(31A)–Zn(2)–N(21)	112.10(13)
N(41B)–Zn(2)–N(21)	130.34(13)	N(31A)–Zn(2)–N(11)	97.80(12)
N(41B)–Zn(2)–N(11)	94.81(12)	N(21)–Zn(2)–N(11)	78.12(12)
N(31A)–Zn(2)–N(5)	94.14(12)	N(41B)–Zn(2)–N(5)	88.47(12)
N(21)–Zn(2)–N(5)	88.14(12)	N(11)–Zn(2)–N(5)	164.42(12)
N(12)–N(11)–Zn(1)	125.2(3)	N(12)–N(11)–Zn(2)	126.4(3)
Zn(1)–N(11)–Zn(2)	100.14(12)	N(13)–N(12)–N(11)	178.8(4)
N(22)–N(21)–Zn(2)	130.1(3)	N(22)–N(21)–Zn(1)	127.4(3)
Zn(2)–N(21)–Zn(1)	102.23(12)	N(23)–N(22)–N(21)	178.5(4)
N(32)–N(31)–Zn(2B)	118.2(3)	N(32)–N(31)–Zn(1)	116.3(2)
Zn(2B)–N(31)–Zn(1)	122.34(14)	N(33)–N(32)–N(31)	179.7(4)
N(42)–N(41)–Zn(1)	118.6(2)	N(42)–N(41)–Zn(2A)	117.3(2)
Zn(1)–N(41)–Zn(2A)	122.98(14)	N(43)–N(42)–N(41)	178.3(4)
C(5)–N(1)–N(2)	106.6(3)	C(5)–N(1)–Zn(1)	133.7(3)
N(2)–N(1)–Zn(1)	114.3(2)	N(3)–N(2)–N(1)	111.9(3)
N(2)–N(3)–N(4)	105.2(3)	C(5)–N(4)–N(3)	109.6(3)
N(3)–N(4)–C(1)	126.2(4)	N(1)–C(5)–N(4)	106.6(3)
C(10)–N(5)–N(6)	106.2(3)	C(10)–N(5)–Zn(2)	128.8(3)
N(6)–N(5)–Zn(2)	117.0(3)	N(7)–N(6)–N(5)	111.8(3)
N(6)–N(7)–N(8)	105.3(3)	C(10)–N(8)–N(7)	109.3(3)
N(7)–N(8)–C(6)	126.2(4)	N(5)–C(10)–N(8)	107.5(3)
C(17)–N(18)–N(19)	104.7(6)	N(18)–C(17)–N(16)	107.5(5)
C(17)–N(16)–N(20)	108.4(5)	N(20)–N(16)–C(21)	129.7(6)
N(19)–N(20)–N(16)	106.9(7)	N(20)–N(19)–N(18)	112.5(6)

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

3. Results and discussion

3.1. Crystal structures

3.1.1. Crystal structure of {[Zn$_2$(N$_3$)$_4$(py-tetrazole)$_2$](py-tetrazole)}$_n$ (1)

The X-ray structure determination for complex **1** revealed that the five coordinate Zn(II) atoms are bridged
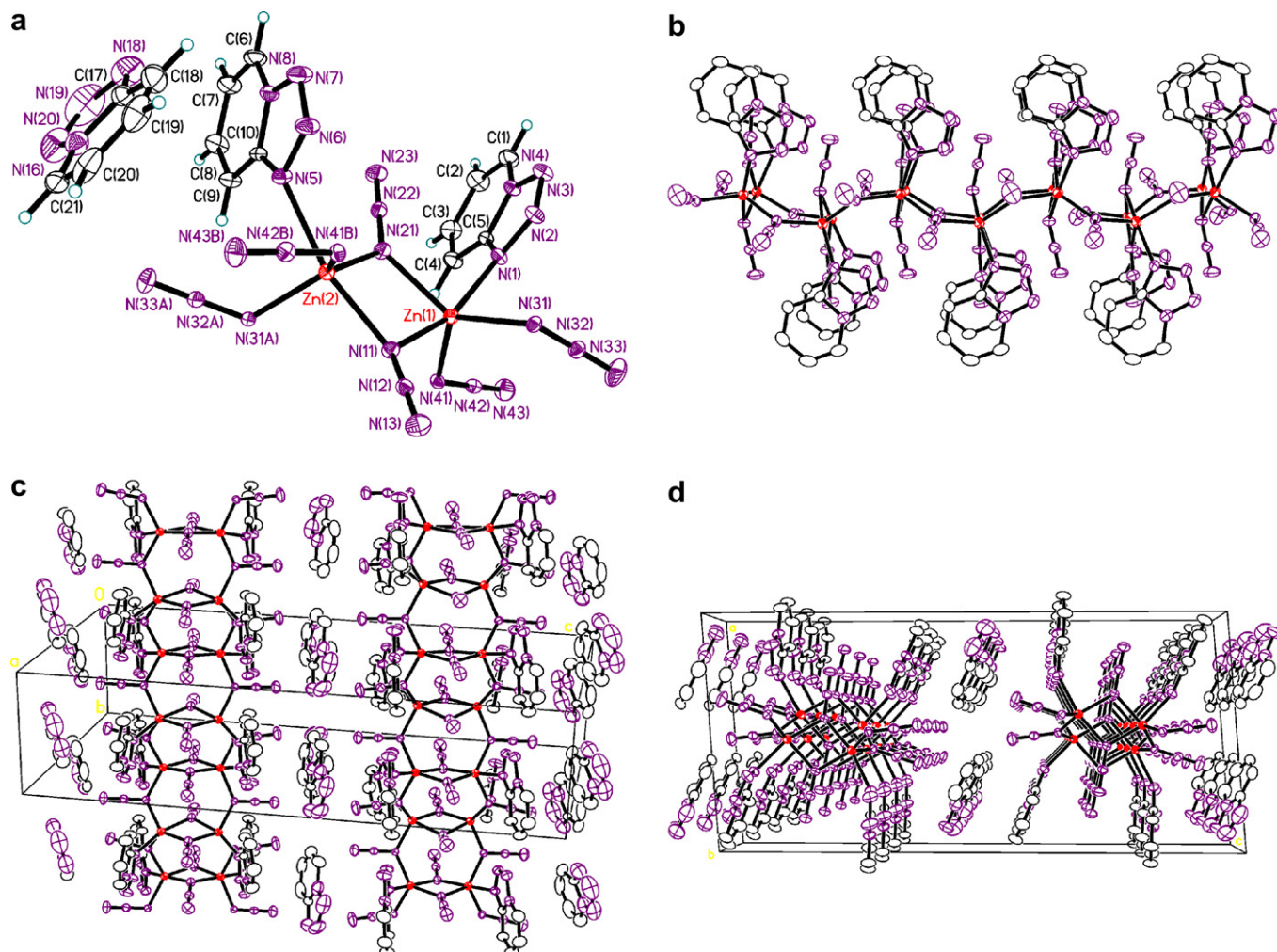
Fig. 1. (a) Perspective view with atom labeling scheme of **1**. Symmetry codes according Table 2. (b) Part of the "ladder-like" arrangement of Zn(II) azide double chains of **1**. (c) Packing view of **1** along the *a*-axis of unit cell. (d) Packing view of **1** along the *b*-axis of unit cell.

by four azido bridges in the EO fashion with a ladder-like arrangement of the 1D zinc(II) azide double chain. A drawing of the asymmetric unit with atom labeling scheme is shown in Figs. 1a–d, show the ladder-like arrangement of the double chain propagated along the crystallographic *b*-axis, and packing plots of the unit cell. Selected bond lengths and bond angles are collected in Table 2. In the coordination chain each zinc(II) ion is coordinated to di-EO azido bridges [Zn(1)–N(11) = 2.087(3), Zn(1)–N(21) = 2.085(3) Å] connecting other Zn(II) ion in the opposite chain forming four-membered Zn_2N_2 cyclic unit [maximum deviation = 0.075(3) Å] crossing the double chain, and two EO bridging azides each on one side of the Zn(II) center [Zn(1)–N(31) = 2.063(3), Zn(1)–N(41). = 2.047(3) Å]. The fifth position is occupied by the nitrogen atom N(1) [Zn(1)–N(1) = 2.252(3) Å] of the tetra-zole ring, leading to the formation of a ZnN_5 chromophore. The stereochemistry around Zn(1) center is intermediate between SP and TBP (τ-value = 0.51), whereas Zn(2) is in a TBP environment (τ-value = 0.56) with N(21), N(31A) and N(41B) in the equatorial positions

and N(5) and N(11) are the axial atoms. As seen from Fig. 1c and d, 4 Zn atoms are interlinked through EO bridging azides giving tetranuclear Zn(II) rings or eight-membered ring and these rings are connected successively to form a ladder of 1D double chain along the *b*-axis. The Zn···Zn distances within the four-membered Zn_2N_2 cyclic units are Zn(1)–Zn(2) = 3.2256(11) Å, whereas the Zn–Zn distances within the eight-membered rings Zn_4N_4 are Zn(1)–Zn(2A) = 3.6003(13) Å and Zn(1)–Zn(2B) = 3.5929(13) Å. In the channels between parallel ladders the py-tetrazole molecules are located Fig. 1c and d. The four bridging azido ligands are asymmetric and almost linear with N–N–N angles from 178.3(4)° to 179.7(4)°, whereas the N(1)–N(2)–N(3) and N(2)–N(3)–N(4) angles of the bonded py-tetrazolate molecule are 111.9(3)° and 105.2(3)°, respectively. The four azido groups show pronounced deviations from linearity in the connection with Zn(II) [Zn–N–N angles from 102.23(12)° to 130.1(3)°]. π–π ring–ring interactions are observed between the five- and six-membered rings of adjacent bicyclic $C_5H_{14}N_4$ molecules (Table 3).

Table 3
Possible ring interactions for **1**

Cg(A)···Cg(B)[a]	Symmetry of ring(B)	Cg(A)···Cg(B) (Å)	Angle (°)[b]
Cg(2)···Cg(4)	x, 1/2 − y, −1/2 + z	4.609(3)	14.7
Cg(2)···Cg(7)	x, 1/2 − y, −1/2 + z	3.687(3)	13.8
Cg(3)···Cg(4)		4.046(4)	32.4
Cg(3)···Cg(7)		4.531(3)	32.6
Cg(4)···Cg(5)	x, 1/2 − y, 1/2 + z	4.381(4)	15.5
Cg(4)···Cg(6)		4.127(4)	31.2
Cg(5)···Cg(7)	x, 1/2 − y, −1/2 + z	3.737(3)	14.6

[a] Cg = center of gravity of ring; ring (2): N(1)–N(4), C(5); ring (3): N(5)–N(8), C(10); ring (4): N(16)–N(19), C(17); ring (5): N(4); C(4)–C(5); ring (6): N(8), C(6)–C(10); ring (7): N(16), C(17)–C(21).
[b] Dihedral angle between planes of rings (A) and (B).

3.1.2. Crystal structure of {[Zn₂(N₃)₄(3-OHpy)] · 2H₂O}ₙ (2)

The principle structure features for complex **2** are illustrated in Fig. 2a, along with a labeling scheme, and selected bond lengths and bond angles are collected in Table 4. The X-ray structure determination of **2** revealed that the Zn(II) atoms are linked by four azido groups all behave in the μ-1,1-EO mode and an oxygen atom from the 3-OH-py ligand which means that this hydroxypyridine molecule acts in the tautomeric keto-form, i.e. as pyridone, in the present complex and bridges two Zn(II) atoms, thus behaving as an *O,O*-bidentate bridging ligand, leading to a 2D system, further carrying into a 3D supramolecular network with the help of several hydrogen bonding interactions. Fig. 2b and c, show the 2D system extented along the *b*- and *c*-axes, and a view of the 2D sheet along the *b*-axis of the unit cell. In the coordination chain each Zn(II) center links another Zn(II) center through a bridging EO azide group and O atom of an *O,O*-pyridone bridge giving rise to a four-membered Zn_2NO ring [Zn(1)–N(11) = 1.996(5) Å and Zn(1)–O(1) = 2.107(4) Å], and links a second Zn center via di-EO bridging azides [Zn(1)–N(21) = 2.054(5) Å] forming a four membered Zn_2N_2 unit [Zn(1)–Zn(2) = 3.2097(11) Å] and finally connects a third Zn(II) atom through an EO azide group. Thus, the zinc center is in a five coordinated environment with a ZnN_4O chromophore. The four-membered ring Zn_2NO deviates from planarity with a max. deviation = 0.063(6) Å for [Zn(1)/O(1)/Zn(2)/N(11)] and a maximum deviation = 0.090(6) Å for [Zn(1)/O(1)/Zn(2D)/N(11)]. The stereochemistry of both Zn centers can be best described as distorted TBP with τ-values of 0.67 and 0.61 for Zn(1) and Zn(2), respectively. Around Zn(1) and Zn(2) the equatorial atoms are N(11), N(31), N(21) and N(11), N(21B), N(41A) and the axial atoms are O(1), N(41) and O(1), N(31A), respectively. As
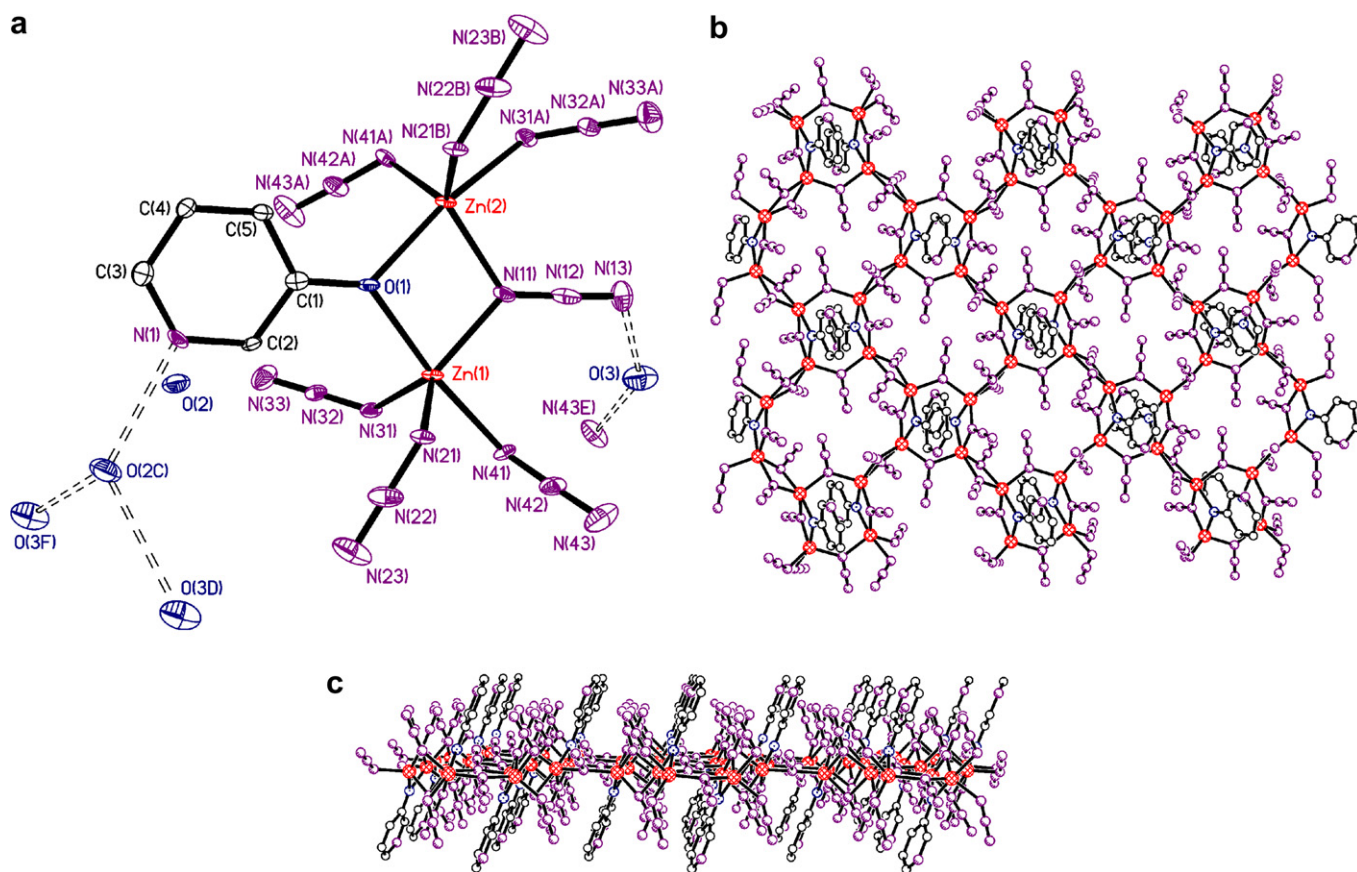

Fig. 2. (a) Perspective view with atom labeling scheme of **2**. Symmetry codes according Table 4. Hydrogen bonds are indicated by broken bonds. (b) 2D system with tetra- and octa-nuclear rings of Zn(II) centers formed by EO-bridging azido and O,O'-bridging pyridones. The 2D system is extented along the *b*- and *c*-axis of the unit cell. (c) View along the *b*-axis of unit cell into a 2D sheet of **2**.

Table 4
Selected bond lengths (Å) and angles (°) for **2**

Zn(1)–N(11)	1.996(5)	Zn(1)–N(31)	2.030(5)
Zn(1)–N(21)	2.054(5)	Zn(1)–O(1)	2.107(4)
Zn(1)–N(41)	2.234(5)	Zn(2)–N(11)	2.028(5)
Zn(2)–N(21B)	2.034(5)	Zn(2)–N(41A)	2.044(5)
Zn(2)–O(1)	2.106(4)	Zn(2)–N(31A)	2.215(5)
N(11)–N(12)	1.249(8)	N(12)–N(13)	1.150(8)
N(21)–N(22)	1.249(8)	N(22)–N(23)	1.149(8)
N(31)–N(32)	1.195(7)	N(32)–N(33)	1.142(8)
N(41)–N(42)	1.214(7)	N(42)–N(43)	1.143(8)
O(1)–C(1)	1.337(8)	N(1)···O(2C)	2.688(8)
Zn(1)···Zn(2)	3.2097(11)	Zn(1)···Zn(2D)	3.2799(11)
Zn(1)···Zn(2B)	3.6318(12)	Zn(1)···Zn(2C)	6.6202(16)
N(11)–Zn(1)–N(31)	128.6(2)	N(11)–Zn(1)–N(21)	118.1(2)
N(31)–Zn(1)–N(21)	113.2(2)	N(11)–Zn(1)–O(1)	77.3(2)
N(31)–Zn(1)–O(1)	99.5(2)	N(21)–Zn(1)–O(1)	96.7(2)
N(11)–Zn(1)–N(41)	95.1(2)	N(31)–Zn(1)–N(41)	78.5(2)
N(21)–Zn(1)–N(41)	94.3(2)	O(1)–Zn(1)–N(41)	168.7(2)
N(11)–Zn(2)–N(21B)	115.2(2)	N(11)–Zn(2)–N(41A)	125.0(2)
N(21B)–Zn(2)–N(41A)	119.8(2)	N(11)–Zn(2)–O(1)	76.7(2)
N(21B)–Zn(2)–O(1)	100.4(2)	N(41A)–Zn(2)–O(1)	94.8(2)
N(11)–Zn(2)–N(31A)	92.9(2)	N(21B)–Zn(2)–N(31A)	97.6(2)
N(41A)–Zn(2)–N(31A)	78.7(2)	O(1)–Zn(2)–N(31A)	161.7(2)
N(12)–N(11)–Zn(1)	127.3(4)	N(12)–N(11)–Zn(2)	124.8(4)
Zn(1)–N(11)–Zn(2)	105.8(2)	N(13)–N(12)–N(11)	178.1(7)
N(22)–N(21)–Zn(2B)	116.1(4)	N(22)–N(21)–Zn(1)	114.6(4)
Zn(2B)–N(21)–Zn(1)	125.4(2)	N(23)–N(22)–N(21)	179.3(7)
N(32)–N(31)–Zn(1)	131.6(4)	N(32)–N(31)–Zn(2D)	127.2(4)
Zn(1)–N(31)–Zn(2D)	101.1(2)	N(33)–N(32)–N(31)	178.9(6)
N(42)–N(41)–Zn(2D)	123.3(4)	N(42)–N(41)–Zn(1)	122.6(4)
Zn(2D)–N(41)–Zn(1)	100.0(2)	N(43)–N(42)–N(41)	178.3(7)
C(1)–O(1)–Zn(2)	130.3(4)	C(1)–O(1)–Zn(1)	130.4(4)
Zn(2)–O(1)–Zn(1)	99.3(2)		

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

can be seen from Fig. 2b, four zinc(II) centers are interconnected by EO azides to afford a tetranuclear ring and eight zinc centers are interconnected to form an octanuclear ring. These two types of rings are the bases for the formation of the 2D sheet. The Zn···Zn distances within the tetranuclear zinc(II) rings are: 3.2097(11) and 3.6318(12) Å; the Zn···Zn separations between opposite pairs of metal centers within the octanuclear zinc(II) rings are in the range from 7.625(2) to 9.714(3) Å. The azide groups are asymmetric and linear [N–N–N angles are from 178.1(7)° to

179.3(7)°], and all of them deviate from linearity in connection with Zn atoms [Zn–N–N angles from 116.1(4)° to 131.6(4)°]. Hydrogen bonds of different types: [O–H···N] between O atom of a lattice water molecule and the end nitrogen atom of an EO azide, or between an oxygen atom of a lattice water and the nitrogen atom of pyridone ligand [N–H···O], and O–H···O between oxygen atoms of lattice water molecules are formed (Table 5). These hydrogen bonds consolidate the structure and lead to the formation of 3D supramolecular network.

Table 5
Hydrogen bonding system for **2**

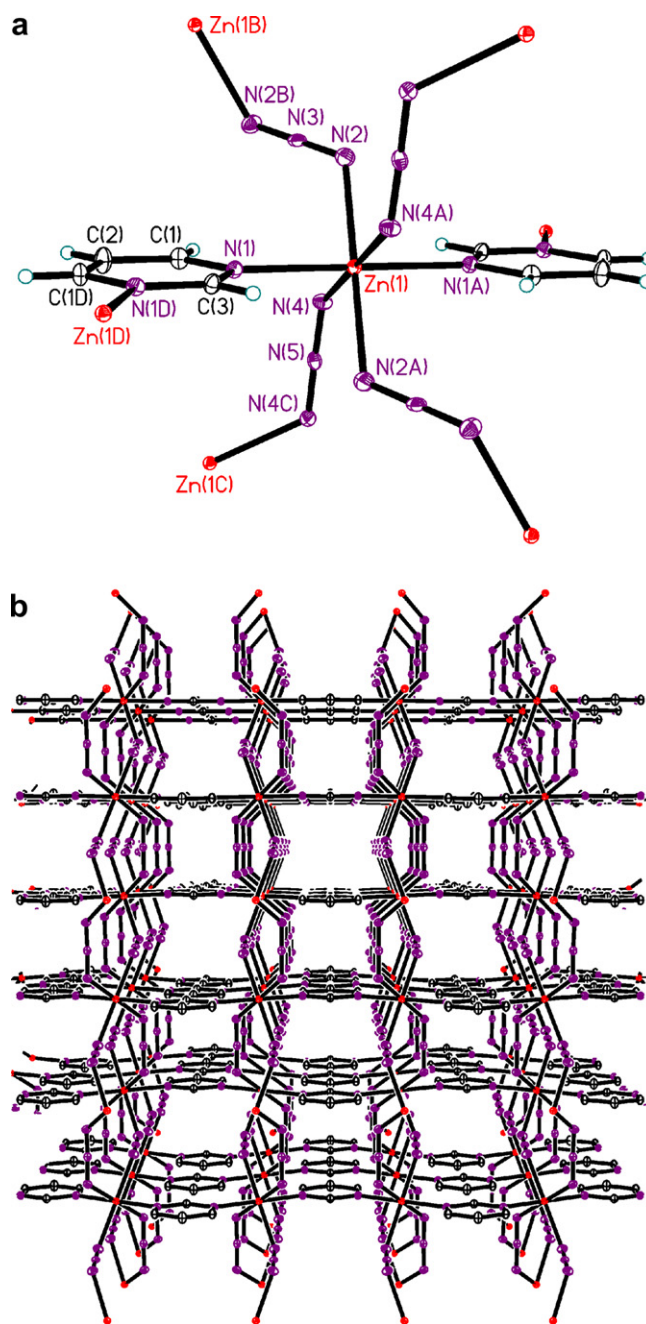| D–H···A[a]	Symmetry of A	D···A (Å)	D–H···A (°)
N(1)–H(1)···O(2)	x, $-1/2 - y$, $1/2 + z$	2.688(8)	171.6
O(2)–H(21)···O(3)	$1 - x$, $-y$, $1 - z$	2.899(8)	156.0
O(2)–H(22)···O(3)	$1 + x$, y, z	2.799(9)	175.7
O(3)–H(31)···N(43)	x, $1/2 - y$, $-1/2 + z$	2.937(9)	140.3
O(3)–H(32)···N(13)		2.970(9)	151.9

[a] D = donor, A = acceptor.

Fig. 3. (a) Perspective view with atom labeling scheme of **3**. Symmetry codes according Table 6. (b) Packing plot of **3** along the *a*-axis of the unit cell.

3.1.3. Crystal structure of $[Zn(N_3)_2(pym)]_n$ (3)

The principle structural features of complex **3** are shown in Fig. 3a, along with a labeling scheme, and selected bond lengths and bond angles are collected in Table 6. The structure features six coordinate Zn(II) atoms, EE bridging azido ligands and N,N'-bidentate bridging pym ligand forming a 3D network. In the asymmetric unit, each Zn(II) center is surrounded by four EE azide bridges [Zn(1)–N(2) = 2.151(3) Å, Zn(1)–N(4) = 2.148(3) Å], and two nitrogen atoms from bidentate N,N'-pyrimidine bridging ligands [Zn(1)–N(1) = 2.188(3) Å] to adopt ZnN_6 chromophore. The 3D system can be seen as zinc-pym chains placed in parallel planes, zinc atoms lie on inversion centers, pym ligands lie across mirror planes and azido ligands lie about 2-fold axes. The four EE azido bridges link each zinc center to two similar chains placed in the upper plane and two similar chains placed in the lower plane. The Zn–N–N bond angles lie around 122.5°. The azido ligands are symmetric [N(2)–N(3) = 1.176(2), N(3)–N(2B) = 1.176(2) Å and N(4)–N(5) = 1.179(2), N(5)–N(4C) = 1.179(2) Å] and linear [N–N–N angles = 178.1(4)° and 179.2(5)°] (Fig. 3b).
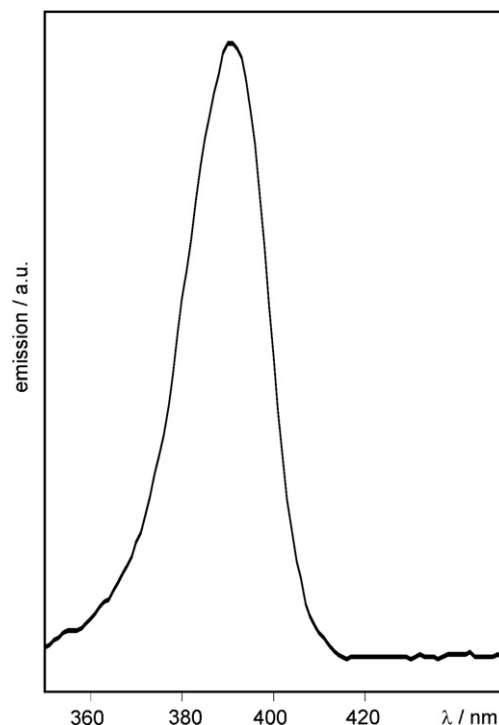
3.2. IR and luminescence spectra

The IR spectra of the title complexes in the solid state exhibit the following very strong band associated with the $v_{as}(N_3)$ vibration mode: 2012, 2098 cm^{-1}; 2121, 2091 cm^{-1}, and 2078 cm^{-1}, for complexes **1**, **2**, and **3**, respectively. The positions of these bands for **1** and **2** with EO azide bridges only are higher than expected [around 2090, 2070 cm^{-1}, and 2100, 2065 cm^{-1} for **1** and **2**, respectively] if the relationship $v_{as}(N_3)$ versus Δd [Δd the difference between the two N–N distances in an azide group] reported earlier [21,22] is valid. The existence of hydrogen bonded lattice water in complex **2** is confirmed by the appearance of broad bands in the range of 3600–2500 cm^{-1}.

Table 6
Selected bond lengths (Å) and angles (°) for **3**

Zn(1)–N(4A)	2.148(2)	Zn(1)–N(4)	2.148(2)
Zn(1)–N(2)	2.151(3)	Zn(1)–N(2A)	2.151(3)
Zn(1)–N(1A)	2.188(3)	Zn(1)–N(1)	2.188(3)
N(2)–N(3)	1.176(2)	N(3)–N(2B)	1.176(2)
N(4)–N(5)	1.179(2)	N(5)–N(4C)	1.179(2)
Zn(1)···Zn(1D)	6.042(2)	Zn(1)···Zn(1B)	5.752(2)
Zn(1)···Zn(1C)	5.588(2)		
N(4A)–Zn(1)–N(4)	180.0	N(4A)–Zn(1)–N(2)	92.16(10)
N(4)–Zn(1)–N(2)	87.84(10)	N(4A)–Zn(1)–N(2A)	87.84(10)
N(4)–Zn(1)–N(2A)	92.16(10)	N(2)–Zn(1)–N(2A)	180.0
N(4A)–Zn(1)–N(1A)	89.79(10)	N(4)–Zn(1)–N(1A)	90.21(10)
N(2)–Zn(1)–N(1A)	87.54(10)	N(2A)–Zn(1)–N(1A)	92.46(10)
N(4A)–Zn(1)–N(1)	90.21(10)	N(4)–Zn(1)–N(1)	89.79(10)
N(2)–Zn(1)–N(1)	92.46(10)	N(2A)–Zn(1)–N(1)	87.54(10)
N(1A)–Zn(1)–N(1)	180.0	N(3)–N(2)–Zn(1)	122.5(2)
N(2)–N(3)–N(2B)	179.2(5)	N(5)–N(4)–Zn(1)	123.6(2)
N(4)–N(5)–N(4C)	178.1(4)		

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

Fig. 4. Luminescence spectrum of **2**.

The photoluminescence properties of the solid zinc(II) complexes have been studied at room temperature. Complexes **1** and **3** do not flouresce, whereas complex **2** exhibits photoluminescence. 3-Hydroxypyridine shows photoluminescence at room temperature with an emission maximum at ca. 390 nm upon excitation at 300 nm. The zinc complex derived from 3-OHpy, **2** exhibits also a strong emission at 390 nm (FWHM: 22 nm) upon excitation at 300 nm (Fig. 4). As Zn(II), Cd(II) and Hg(II) are not easily oxidize or reduce due to their electronic d^{10} configuration, no emission originated from metal centers excited states are expected in case of such cations. Thus the flourescence observed in case of complex **2** is assigned to the intra-ligand flourescence [23,24]. The complexation of the ligands may also increase the rigidity and reduces the loss of energy by thermal vibrational decay. However, 3-OHpy from which complex **2** is derived, in the solid state exist in the keto and enol tautomers, and its flourescence is due to both tautomeric forms. In complex **2**, the 3-OHpy exists only in the keto form, in which the pair of electron remain as in the free ligand. This may explain why both 3-OHpy and its Zn(II) azide complex fluoresce almost at the same wavelength maximum, except that the intensity of the flourescence of the complex is more than twice the intensity of the free 3-OHpy ligand.

4. Discussion

Three zinc(II) azido complexes of three different ligands have been synthesized. In fact the ligand tetrazolo[1,5-*a*]pyridine (py-tetrazole) was prepared through the interac-
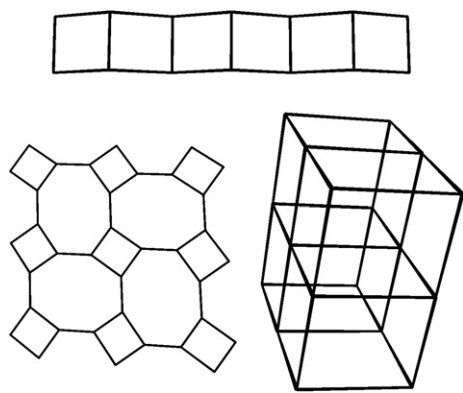
Fig. 5. Simplified representation of the structural motifs observed in complexes **1** (ladder, 1D), **2** (rings, 2D) and **3** (cubes, 3D).

tion of 2-chloropyridine with azide N_3^- ion under hydro-thermal conditions, as given in Scheme 1; the py-tetrazole then interacts with zinc(II) azide affording complex **1**. In the case of complex **2**, we started with 3-hydroxypyridine, under reaction condition this ligand seems to prefer to be in the tautomeric keto-form, and we obtained a complex containing the pyridone which behaves as an *O,O*-biden-tate bridging ligand. As we have seen the structure of complex **1** consists of a ladder-like arrangement in which four zinc centers interconnect through EO bridging azide forming tetranuclear rings and the uncoordinated py-tetrazole molecules are located in the channels between the parallel ladders. This structure is unprecedented in metal azido complexes. The structure of complex **2**, on the other hand, consists of tetranuclear zinc(II) rings fused with octanuclear zinc(II) rings forming 2D sheets, which is carrying into 3D network through the hydrogen bonding interaction. This structure too is unprecedented in known metal azido complexes (Fig. 5). In both complexes **1** and **2** with EO azide bridges only, the Zn–Zn distances within the Zn_2N_2 cyclic units fall well within the range of 3.03–3.31 Å found for other zinc(II) azido complexes containing such units [25]. All EO bridging azides in both complexes are asym-metric [the two N–N lengths within the azide group are dif-ferent] and linear as reported earlier [26]. Complex **3** contains only EE bridging azido ligands which are symmet-rical and linear as usual [26], and its structure resembles that of manganese(II) azide with pyrimidine [27]. In terms of network analysis [28] the topology of **2** may be described as a distorted "4.8^2" 2D net [the lengths of the edges within the tetranuclear rings are 3.210 and 3.632 Å, respectively, and additionally 3.280 Å in the octanuclear rings (Fig. 5, bottom left)]; the topology of **3** as distorted "α-Po" 3D net [the lengths of the edges of the cubes are 5.588, 5.752 and 6.042 Å, respectively (Fig. 5, bottom right)].

5. Conclusions

We isolated three zinc(II) azide complexes with some pyridines and pyrimidine by hydrothermal technique.

Although we started with 2-chloropyridine which interacts with the azide ion forming py-tetrazole ligand and the iso-lated complex found to be $\{[Zn(N_3)_4(py\text{-tetrazole})_2](py\text{-tet-razole})\}_n$ (**1**) which links the zinc ion not through the pyridine nitrogen atom but via a nitrogen atom from the tetrazole part. The ladder-like structure of this complex contains tetranuclear zinc(II) rings. This structure is unprecedented. In complex **2**, the 3-Ohpy, starting reactant found to behave in the tautomeric keto-form and ligated zinc atoms as *O,O*-bidentate bridging ligand, in addition to the existence of tetranuclear zinc(II) and octanuclear zinc(II) rings fused together to generate 2D sheets which carrying into 3D supramolecular network with the help of hydrogen bonding. This complex exhibits photolumines-cence at room temperature, and is unprecedented too in the metal azide complexes. Complex **3** consists of three-dimen-sional network. These results prompted us to explore the synthesis of zinc and other metal complexes with 2-, and 4-hydroxypyridines as well as other 2-X-pyridines in pres-ence of azide ion and to explore the photoluminescence of the isolated complexes. Such reactions are under current investigation.

Supplementary data

CCDC 660643, 660644 and 660645 contain the supple-mentary crystallographic data for compounds **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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