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1D and 2D Systems Derived from Polynuclear $[ML(N_3)_2]_n$ (M = Zn(II) or Cd(II) and L is 2-Picoline-*N*-oxide or 4-Methylpyrimidine)

Franz A. Mautner[1,*], **Christian Gspan**[1], **Mohamed A. S. Goher**[2], and **Morsy A. M. Abu-Youssef**[2]

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

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Summary. Four new polynuclear complexes: $[Zn(2picNO)(N_3)_2]_n$, $[Zn(4Mepym)(N_3)_2]_n$, $[Cd(2picNO)(N_3)_2]_n$, and $[Cd(4Mepym)(N_3)_2]_n$ (*2picNO* = 2-picoline-*N*-oxide and *4Mepym* = 4-methylpyrimidine) have been synthesized and characterized by single-crystal X-ray diffraction. The structures of the zinc(II) complexes feature five-coordinate zinc atoms, (μ-1,1) azido bridges, monodentate organic ligands, and 1D chains. The cadmium(II) azide complexes contain distorted octahedral metal atoms linked by alternate di-(μ-1,1) and di-(μ-1,3) azido bridges in *cis* arrangement and these chains are connected by *2picNO* bridges giving a honeycomb 2D framework or by *4Mepym* bridges forming extended 2D network structure.

Keywords. IR spectroscopy; 1D zinc(II) and cadmium(II) azido complexes; Pyridine derivative ligands; Synthesis; X-Ray structure determination.

Introduction

The construction of polymeric coordination network is an extremely topical area of research [1, 2] and a wide variety of network topologies has been constructed through ligand design and the use of different transition metal coordination geometries. These include infinite one-, two-, and three-dimensional systems including helical [3], diamondoid and honeycomb [4], square [5], or rectangular [6] grid and other uncommon frameworks. As part of our investigation on polymeric coordination networks constructed through the versatile azido, thiocyanato, and cyanato

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[*] Corresponding author. E-mail: mautner@ptc.tu-graz.ac.at

ligands and as the cadmium(II) azide complexes are very few [7–12], we recently reported a number of polymeric complexes of cadmium(II) azide with some pyridine derivatives formulated as Cd(*L*)(N_3)$_2$ for *L* = *2acpy*, *3CNpy*, Cd(*L*)$_2$(N_3)$_2$ for *L* = *4acpy*, *35lut*, *3aldpy* (with an aqua molecule), and Cd_3(*4Brpy*)$_4$(N_3)$_6$ (were *acpy* = acetylpyridine, *CNpy* = cyanopyridine, *lut* = lutidine, *aldpy* = pyridinealdehyde, *Brpy* = bromopyridine) [13–15]. The structure determinations of these complexes revealed a variety of cadmium(II) azide topologies and different modes of azide bridges. When we used pyridine-*N*-oxide or 3-picoline-*N*-oxide (*pyNO* or *picNO*, respectively) to interact with zinc(II) azide or cadmium(II) azide we isolated polymeric complexes containing non-coordinated *pyNO* or *picNO* [16]. As a consequence of this difference, we extended our work using 2-picoline-*N*-oxide (*2picNO*) and 4-methylpyrimidine (*4Mepym*) to interact with zinc(II) azide and cadmium(II) azide.

Results and Discussions

Crystal Structures

Figure 1 illustrates the principle structural features of complex **1**, selected bond lengths and bond angles are listed in Table 1. The structure features five coordinate zinc(II). Each zinc atom is linked by four nitrogen atoms, N(11), N(21), N(31), and N(41) from two (μ-1,1) bridging azides [Zn–N from 199.2 to 223.9 pm] forming cyclic Zn_2N_2 units. The fifth coordinate site of the zinc atom is occupied by oxygen atom O(1) or O(2) of a mono-dentate 2-picoline-*N*-oxide ligand. The stereochemistry about Zn(1) ($\tau = 0.656$) and Zn(2) ($\tau = 0.735$) may be described as distorted trigonal bipyramid with N(11) and N(41), respectively N(21) and N(31A) in the apical positions. The 1D chains of polyhedra are directed along the *a*-axis of the unit cell. The structure of complex **1**, resembles that of corresponding [Cu(*2picNO*)(N_3)$_2$]$_n$ [17] with subtle differences. The copper complex crystallizes in *P*-1 (no. 2) space group, the stereochemistry about each copper atom is distorted square pyramid and the N–O–Cu angle is 115.3(2)° compared with 119.5(4)° in

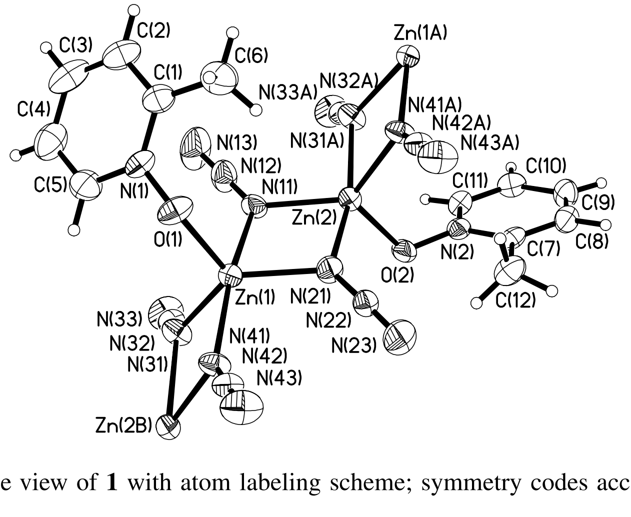

Fig. 1. Perspective view of **1** with atom labeling scheme; symmetry codes according to Table 1

Table 1. Selected bond lengths/pm and angles/° of **1**

Zn(1)–O(1)	198.1(6)	Zn(1)–N(21)	199.2(5)
Zn(1)–N(31)	202.1(6)	Zn(1)–N(41)	216.6(5)
Zn(1)–N(11)	223.9(5)	Zn(2)–O(2)	196.8(6)
Zn(2)–N(11)	201.8(5)	Zn(2)–N(41A)	202.2(6)
Zn(2)–N(21)	219.2(5)	Zn(2)–N(31A)	225.0(5)
N(11)–N(12)	119.3(8)	N(12)–N(13)	115.4(8)
N(21)–N(22)	121.4(7)	N(22)–N(23)	112.5(7)
N(31)–N(32)	120.1(8)	N(32)–N(33)	114.1(9)
N(41)–N(42)	121.1(8)	N(42)–N(43)	112.7(9)
Zn(1)..Zn(2)..Zn(1A)	138.70(4)	O(1)–Zn(1)–N(21)	117.3(3)
O(1)–Zn(1)–N(31)	113.9(2)	N(21)–Zn(1)–N(31)	128.7(3)
O(1)–Zn(1)–N(41)	95.8(2)	N(21)–Zn(1)–N(41)	98.0(2)
N(31)–Zn(1)–N(41)	80.2(2)	O(1)–Zn(1)–N(11)	96.0(2)
N(21)–Zn(1)–N(11)	78.2(2)	N(31)–Zn(1)–N(11)	93.3(2)
N(41)–Zn(1)–N(11)	168.1(3)	O(2)–Zn(2)–N(11)	121.1(3)
O(2)–Zn(2)–N(41A)	113.3(2)	N(11)–Zn(2)–N(41A)	125.5(3)
O(2)–Zn(2)–N(21)	99.3(2)	N(11)–Zn(2)–N(21)	78.7(2)
N(41A)–Zn(2)–N(21)	96.8(2)	O(2)–Zn(2)–N(31A)	95.4(2)
N(11)–Zn(2)–N(31A)	92.7(2)	N(41A)–Zn(2)–N(31A)	78.2(2)
N(21)–Zn(2)–N(31A)	165.2(2)	N(12)–N(11)–Zn(2)	124.4(5)
N(12)–N(11)–Zn(1)	134.7(5)	Zn(2)–N(11)–Zn(1)	100.3(2)
N(13)–N(12)–N(11)	179.2(10)	N(22)–N(21)–Zn(1)	123.9(4)
N(22)–N(21)–Zn(2)	133.4(4)	Zn(1)–N(21)–Zn(2)	102.7(2)
N(23)–N(22)–N(21)	178.2(9)	N(32)–N(31)–Zn(1)	124.8(4)
N(32)–N(31)–Zn(2B)	133.1(5)	Zn(1)–N(31)–Zn(2B)	99.1(2)
N(33)–N(32)–N(31)	178.2(8)	N(42)–N(41)–Zn(2B)	119.6(4)
N(42)–N(41)–Zn(1)	138.4(5)	Zn(2B)–N(41)–Zn(1)	102.0(3)
N(43)–N(42)–N(41)	178.7(8)	N(1)–O(1)–Zn(1)	118.9(4)
N(2)–O(2)–Zn(2)	119.5(4)		

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

the present complex. The (μ-1,1) bridging azides are asymmetric with Δd (Δd is the difference between N_a–N_β and N_β–N_y) varying from 39 to 84 pm.

The structural features of complex **2** are shown in Fig. 2, and bond parameters are given in Table 2. Each five coordinate Zn(1) ($\tau = 0.457$) is coordinated by five nitrogen atoms, N(11), N(11A), N(21), N(21B) [Zn–N from 204.7 to 212.2 pm] from two (μ-1,1) azide bridges and N(1) [Zn–N 206.5(2) pm] from a mono-dentate *4Mepym* ligand. The 1D chain of polyhedra is directed along the *a*-axis of the unit cell. Both azido bridges are linear and asymmetric [N(11)–N(12) 120.6(3), N(12)–N(13) 114.3(4) pm and N(21)–N(22) 120.7(3), N(22)–N(23) 114.2(4) pm].

The atom labeling scheme for complex **3** is shown in Fig. 3. Selected bond distances and bond angles are gathered in Table 3. The structure consists of a 2D layer of octahedral centrosymmetric cadmium atoms linked by azide and 2-picoline-*N*-oxide. Each cadmium atom is bridged by alternating di-(μ-1,1) [Cd–N = 231.0(5), 230.8(5) pm] and di-(μ-1,3) [Cd–N = 230.0(5), 236.2(5) pm] forming two cyclic units, Cd_2N_2 and $Cd_2(NNN)_2$. The other two coordination sites

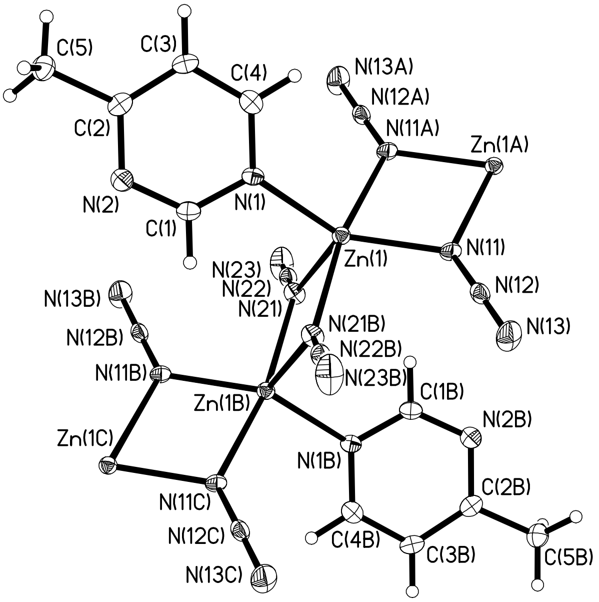

Fig. 2. Molecular structure and atom labeling scheme of **2**

Table 2. Selected bond lengths/pm and angles/° of **2**

Zn(1)–N(11)	204.7(2)	Zn(1)–N(21)	205.0(2)
Zn(1)–N(1)	206.5(2)	Zn(1)–N(11A)	212.2(2)
Zn(1)–N(21B)	216.1(2)	N(11)–N(12)	120.6(3)
N(12)–N(13)	114.3(4)	N(21)–N(22)	120.7(3)
N(22)–N(23)	114.2(4)		
Zn(1A)..Zn(1)..Zn(1B)	135.54(3)	N(11)–Zn(1)–N(21)	116.89(9)
N(11)–Zn(1)–N(1)	141.77(9)	N(21)–Zn(1)–N(1)	101.33(9)
N(11)–Zn(1)–N(11A)	76.93(10)	N(21)–Zn(1)–N(11A)	102.96(9)
N(1)–Zn(1)–N(11A)	96.10(9)	N(11)–Zn(1)–N(21B)	92.74(9)
N(21)–Zn(1)–N(21B)	78.69(10)	N(1)–Zn(1)–N(21B)	94.02(9)
N(11A)–Zn(1)–N(21B)	169.19(8)	N(12)–N(11)–Zn(1)	124.9(2)
N(12)–N(11)–Zn(1B)	130.4(2)	Zn(1)–N(11)–Zn(1B)	103.07(10)
N(13)–N(12)–N(11)	178.7(3)	N(22)–N(21)–Zn(1)	128.5(2)
N(22)–N(21)–Zn(1B)	130.1(2)	Zn(1)–N(21)–Zn(1B)	101.31(10)
N(23)–N(22)–N(21)	179.3(3)		

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

of cadmium in *cis*-position to each other are occupied by oxygen atoms of two partially disordered *2picNO* bridges. That each pair of (μ-1,1) and (μ-1,3) azide nitrogen atoms and oxygen atoms of the μ-O,O ligand are coordinated to a cadmium atom in *cis*-arrangement gives rise to a Cd_6 honeycomb structure (Fig. 4). The chair conformation angle is 11.4(2)° and the out of plane angle of N(11)–N(12)–N(13) azide group is 19.2(5)°. The structure thus contains three types of rings; two four membered rings, Cd_2N_2, Cd_2O_2, and eight membered rings $Cd_2(NNN)_2$, with intra-ring Cd–Cd distances of 369.2(2), 386.0(2), and 557.7(3) pm,

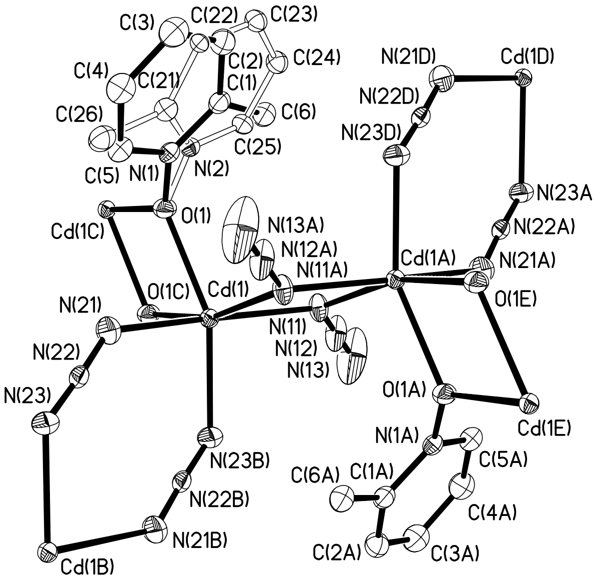

Fig. 3. Molecular structure and atom labeling scheme of **3**; the orientation with minor occupancy of disordered *2picNO* ligand is indicated by open stick bonds; symmetry codes according to Table 3

Table 3. Selected bond lengths/pm and angles/° for **3**

Cd(1)–N(23B)	230.0(5)	Cd(1)–N(11A)	230.8(5)
Cd(1)–N(11)	231.0(4)	Cd(1)–O(1)	231.4(3)
Cd(1)–O(1E)	233.8(3)	Cd(1)–N(21)	236.2(5)
N(11)–N(12)	119.1(7)	N(12)–N(13)	114.6(9)
N(21)–N(22)	116.7(6)	N(22)–N(23)	117.8(6)
Cd(1A)..Cd(1)..Cd(1B)	120.53(3)	Cd(1A)..Cd(1)..Cd(1E)	123.76(4)
Cd(1B)..Cd(1)..Cd(1E)	115.27(4)	N(23B)–Cd(1)–N(11A)	109.5(2)
N(23B)–Cd(1)–N(11)	91.6(2)	N(11A)–Cd(1)–N(11)	75.5(2)
N(23B)–Cd(1)–O(1)	151.47(14)	N(11A)–Cd(1)–O(1)	98.4(2)
N(11)–Cd(1)–O(1)	101.2(2)	N(23B)–Cd(1)–O(1E)	85.1(2)
N(11a)–Cd(1)–O(1E)	164.17(14)	N(11)–Cd(1)–O(1E)	98.75(14)
O(1)–Cd(1)–O(1E)	67.9(2)	N(23B)–Cd(1)–N(21)	90.3(2)
N(11A)–Cd(1)–N(21)	88.4(2)	N(11)–Cd(1)–N(21)	163.4(2)
O(1)–Cd(1)–N(21)	84.7(2)	O(1E)–Cd(1)–N(21)	97.8(2)
N(12)–N(11)–Cd(1A)	123.8(4)	N(12)–N(11)–Cd(1)	126.6(4)
Cd(1A)–N(11)–Cd(1)	104.5(2)	N(13)–N(12)–N(11)	179.2(8)
N(22)–N(21)–Cd(1)	138.7(4)	N(21)–N(22)–N(23)	176.9(5)
N(22)–N(23)–Cd(1B)	124.4(4)	N(1)–O(1)–Cd(1)	122.3(2)
N(2)–O(1)–Cd(1)	123.93(13)	N(1)–O(1)–Cd(1E)	125.29(13)
N(2)–O(1)–Cd(1E)	120.2(2)	Cd(1)–O(1)–Cd(1E)	112.1(2)
N(12)–N(11)..N(11A)	160.2(5)		

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

respectively. The bond lengths and bond angles at the cadmium centre are typical for azide and oxygen-coordination. The angle between the plane of the four-membered rings, Cd_2N_2 and Cd_2O_2, is 79.45(14)°. The two dimensional

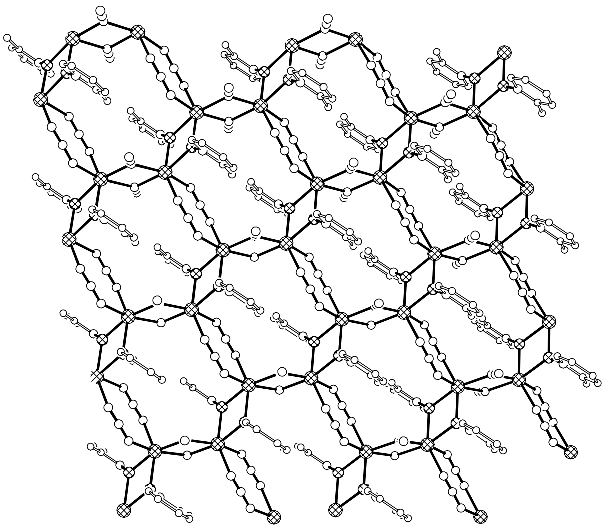

Fig. 4. $[Cd(2picNO)(N_3)_2]_n$ (**3**): Cd(II)-azido chains with alternating EO- and EE-bridging sequence are connected by the *2picNO* ligands to form a honeycomb like layer system

Cd_6 honeycomb structure of the present complex is the first to have been observed in reported cadmium azide complexes.

Complex **4** crystallizes in the monoclinic space group $P2_1/n$ and consists of a 2D cadmium azido pyrimidine network (Figs. 5, 6). Each cadmium atom is coordinated in a distorted octahedral environment by four azide nitrogen atoms [Cd–N from 227.7 to 234.5 pm] and two other pyrimidine nitrogen atoms [Cd–N 233.4(4) and 241.3(4) pm] (Table 4). The azido ligands function in (μ-1,1) and (μ-1,3) bridging modes, and each cadmium atom is linked by alternating di-(μ-1,1) and

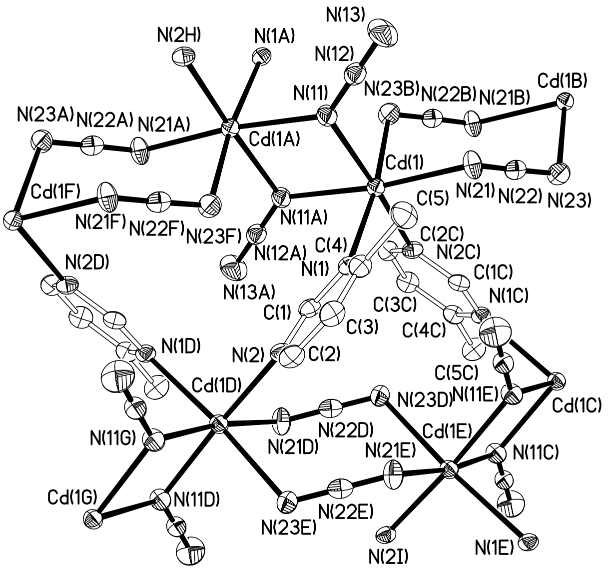

Fig. 5. Molecular structure and atom labeling scheme of **4**; symmetry codes according to Table 4

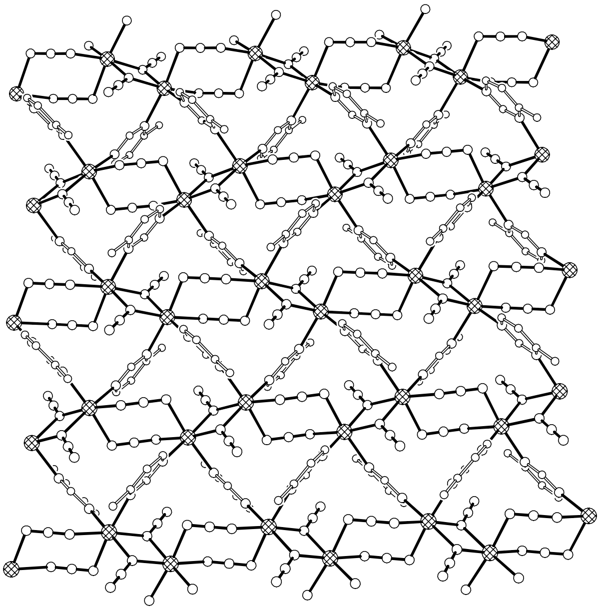

Fig. 6. 2D layer system of $[Cd(4Mepym)(N_3)_2]_n$ (**4**)

Table 4. Selected bond lengths/pm and angles/° of **4**

Cd(1)–N(11)	227.7(4)	Cd(1)–N(21)	229.5(4)
Cd(1)–N(2C)	233.4(4)	Cd(1)–N(11A)	234.5(4)
Cd(1)–N(1)	241.3(4)	Cd(1)–N(23B)	243.5(4)
N(11)–N(12)	120.6(6)	N(12)–N(13)	115.0(6)
N(21)–N(22)	117.9(6)	N(22)–N(23)	118.0(6)
Cd(1A)..Cd(1)..Cd(1B)	132.19(3)	N(11)–Cd(1)–N(21)	96.02(14)
N(11)–Cd(1)–N(2C)	170.44(14)	N(21)–Cd(1)–N(2C)	90.74(14)
N(11)–Cd(1)–N(11A)	81.03(14)	N(21)–Cd(1)–N(11A)	172.87(14)
N(2C)–Cd(1)–N(11A)	91.46(14)	N(11)–Cd(1)–N(1)	88.90(14)
N(21)–Cd(1)–N(1)	99.30(14)	N(2C)–Cd(1)–N(1)	96.69(13)
N(11A)–Cd(1)–N(1)	87.17(14)	N(11)–Cd(1)–N(23B)	88.87(14)
N(21)–Cd(1)–N(23B)	87.6(2)	N(2C)–Cd(1)–N(23B)	84.66(14)
N(11A)–Cd(1)–N(23B)	85.83(14)	N(1)–Cd(1)–N(23B)	172.91(13)
N(12)–N(11)–Cd(1)	121.3(3)	N(12)–N(11)–Cd(1A)	136.1(3)
Cd(1)–N(11)–Cd(1A)	98.97(14)	N(13)–N(12)–N(11)	179.3(5)
N(22)–N(21)–Cd(1)	125.3(3)	N(21)–N22)–N(23)	176.7(5)
N(22)–N(23)–Cd(1B)	114.2(3)	N(12)–N(11)–N(11A)	163.0(4)

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

di-(μ-1,3) azides giving rise to a one dimensional cadmium-azide chain along *b*-axis of the unit cell with alternate four-membered Cd_2N_2 and eight-membered $Cd_2(NNN)_2$ rings. Each 4-methylpyrimidine ligand acts as a bidentate bridge connecting the cadmium azido chains along [101], extending the structure to a 2D network. The chair conformation angle of 44.4(2)° is much greater than in complex **3**, whereas the out of plane angle of N(11)–N(12)–N(13) of 17.0(4)° is comparable with the corresponding angle in **3**. The angle between N(1)–C(5) of a *4Mepym* ligand to N(1C)–C(5C) of a second *4Mepym* ligand is 87.78(12)°. The Cd–N(azide) bond lengths are a little longer in the present complex than corresponding values in **3**, what may be due to the different nature of the bridging *2picNO* connecting to successive metal atoms and *4Mepym* linking parallel chains.

Discussion

The interaction of zinc(II) azide and cadmium(II) azide with *2picNO* and *4Mepym* afforded the title complexes. As it can be seen, in both zinc azide and cadmium azide complexes, *2picNO* acts as a monodentate ligand in **1** and as a bidentate ligand in **3**, and therefore they differ from those of *pyNO* or *3picNO* [16] containing non-coordinated organic molecules. Complexes **1**–**4** are insoluble in many polar or non-polar solvents, but they are soluble in *DMSO*. As we found for other cadmium(II) azide complexes [15] the ^{1}H NMR spectra of both zinc and cadmium complexes revealed a complete substitution of the azides by *DMSO* molecules.

Complexes **1** and **2** contain only (μ-1,1) azide bridges and this is revealed by the appearance of two very strong bands at 2101, 2060 cm^{-1}, and 2106, 2055 cm^{-1}, and two weak to medium bands at 1347, 1296 cm^{-1}, and 1385, 1291 cm^{-1}, respectively, in their IR spectra. These bands are due to asymmetric and symmetric stretching modes, respectively, and are consistent with asymmetric (μ-1,1) azide bridges [17, 18]. The azide asymmetric stretching mode for complexes **3** and **4** appears at lower frequencies 2082, 2039 cm^{-1} and 2047 cm^{-1} (broad), respectively. The higher frequency band in **3** may be due to (μ-1,1) bridging azides whereas the lower frequency band is due to (μ-1,3) azide bridges similar to that reported for $[Cd(pyridine)_2(N_3)_2]_n$ with only (μ-1,3) azides [8]. That the $\nu_{as}(N_3)$ mode appears at lower frequencies in spectra of cadmium complexes suggests that the μ-1,1 azide bridges are less asymmetric (smaller difference in N–N bonds in azide groups) in **3** and **4** than in zinc(II) complexes **1** and **2**.

It is noteworthy to compare complex **2** with known zinc(II) azide complexes of the same formula $[ZnL(N_3)_2]_n$ for $L = 2$-picoline [19], 3-picoline [20], 4-picoline [21], and lutidines [22]. All these six structures are very similar featuring ZnN_5 geometries with distorted trigonal bipyramids. The asymmetric end-on (μ-1,1) azide bridges are forming 1D chains with common edges, with one equatorial Zn–N bond [from 199 to 205 pm, mean value 202 pm] and one longer axial Zn–N bond [range 211 to 228 pm, mean value 222 pm], respectively. Due to low steric hindrance of the azide bridges the difference of axial and equatorial Zn–N bonds of 20 pm is in good agreement with theoretical calculation done for d^{10} systems by *Gillespie* [23]. In all the above six complexes the Zn–N(pyridine) bond range is 199 to 206 pm (mean value 202 pm), the Zn..Zn distances range from 303 to 331 pm and Zn..Zn..Zn angles from 134 to 140°.

Although complexes **3** and **4** adopt different structures, both structures, however, differ from that of [Cd(*3CNpy*)$(N_3)_2]_n$ (**5**) which contains also six-coordinate cadmium centers [15]. In the structure of **5** each pair of adjacent cadmium atoms are bridged by a pair of (μ-1,1) azide groups forming 1D $[Cd(N_3)_2]_n$ chains, and these chains are further connected by N,N′-bridging *3CNpy* ligands generating a 2D system.

Conclusion

2picNO is acting as monodentate or O,O′-bridging bidentate ligand in its Zn(II) or Cd(II) azide complexes, whereas under similar aqueous conditions *3picNO* and *pyNO* molecules act as lattice molecules and are not ligated to the metal centers. Thus it is evident that the small electronic change caused by the methyl-substituent in *ortho*-position of the pyridine ring is improving the O-donor strength of the *2picNO* ligand to prevent the substitution of the latter N-oxides by solvent water molecules in the coordination sphere of the metal centers.

Experimental

Materials and Instrumentations

Elemental analyses of C, H, N were carried out using a Perkin Elmer analyzer, Zn and Cd by complexometric titration; results were in good agreement with calculated values. IR spectra were recorded on a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets. ^{1}H NMR and ^{13}C NMR (*DMSO*-d$_6$) spectra were recorded on a Jeol JNM-ECA 500 MHz spectrometer. 2-Picoline-*N*-oxide and 4-methylpyrimidine have been purchased from Aldrich company and other chemicals were of analytical grade quality and used as received.

Caution: Metal azide complexes are potentially explosives. Only a small amount of material should be prepared and should be handled with caution.

[Zn(2-picoline-N-oxide)(N$_3$)$_2$]$_n$ (**1**, $C_{12}H_{14}N_{14}O_2Zn_2$)

The complex was prepared by solving 0.97 g of 2-picoline-*N*-oxide (8.9 mmol) in 10 cm^3 of an aqueous solution of $Zn(N_3)_2$ (8.9 mmol), saturated with hydrazoic acid [24]. The solution was allowed to stand in a refrigerator for several hours to produce brown crystals of the complex. Yield 1.49 g (65%); IR (KBr): $\bar{\nu} = 2101$, 2060, 1486, 1456, 1347, 1296, 1208, 1110, 988, 845, 772, 698, 663, 599 cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.34$ (s, 3H), 7.32 (m, 2H), 7.46 (d, 1H), 8.25 (d, 1H) ppm; ^{13}C NMR (*DMSO*-d$_6$): $\delta = 17.74$, 124.66, 127.42, 127.80, 139.92, 149.15 ppm.

[Zn(4-methylpyrimidine)(N$_3$)$_2$]$_n$ (**2**, $C_5H_6N_8Zn$)

A similar preparation method was used as for **1** with 4-methylpyrimidine (1.40 g, 14.9 mmol) as ligand. Colorless transparent crystals were obtained from the clear solution after several hours. Yield 1.30 g (60%); IR (KBr): $\bar{\nu} = 2635$, 2106, 2055, 1605, 1537, 1476, 1385, 1291, 847, 831, 845, 734, 670, 596, 568, 492 cm^{-1}.

[Cd(2-picoline-N-oxide)(N$_3$)$_2$]$_n$ (**3**, $C_6H_7CdN_7O$)

This complex was prepared by mixing $3CdSO_4 \cdot 8H_2O$ (0.5 g, 1.95 mmol Cd) in water (20 cm^3) with 2-picoline-*N*-oxide (2.70 g, 24.7 mmol), NaN_3 (0.325 g, 5 mmol, in 5 cm^3 of H_2O) and 6 cm^3 of aqueous hydrazoic acid. The final clear solution was allowed to stand for several days to deposit brown crystals of the complex suitable for X-ray measurements. Yield 0.36 g (60%); IR (KBr): $\bar{\nu} = 2082$, 2039, 1490, 1457, 1333, 1284, 1201, 1113, 1041, 995, 842, 776, 697, 654, 594, 551 cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.33$ (s, 3H), 7.29 (bs, 2H), 7.44 (d, 1H), 8.26 (bs, 1H) ppm; ^{13}C NMR (*DMSO*-d$_6$): $\delta = 17.78$, 124.56, 126.91, 127.28, 139.85, 148.97 ppm; free *DMSO* shifts: $\delta = 40.07$ (multiplett strong) ppm and coordinated *DMSO* shifts: $\delta = 13.80$ (multiplett very week) ppm (This multiplett appears only when the sample was scanned for 24 hours).

[Cd(4-methylpyrimidine)$(N_3)_2$]$_n$ (**4**, $C_5H_6CdN_8$)

A similar preparation method was used as for **3** with 4-methylpyrimidine (0.24 g, 2.5 mmol) as ligand. Colorless transparent crystals were obtained after allowing the clear solution to stand in a refrigerator for several days. Yield 0.40 g (70%); IR (KBr): $\bar{\nu} = 2047$, 1610, 1389, 1332, 1305, 1283, 1163, 1085, 1225, 860, 828, 733, 683, 650, 626, 598, 565, 494 cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.41$ (s, 3H), 7.40 (d, 1H), 8.55 (d, 1H), 8.95 (s, 1H) ppm; ^{13}C NMR (*DMSO*-d$_6$): $\delta = 24.14$, 121.95, 156.71, 158.35, 168.43 ppm.

X-Ray Crystallography

Single crystal X-ray data were measured on a modified *STOE* four circle diffractometer at 90(2) K (except for **1** at RT) using graphite crystal-monochromatized Mo-Kα radiation ($\lambda = 71.069$ pm). The intensities were corrected for *Lorentz*-polarisation effects and for absorption [range of transmission factors: 0.627–0.816, 0.564–0.746, 0.557–0.832, and 0.548–0.820, for **1**–**4**, respectively]. Crystallographic data and processing parameters are given in Table 5.

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. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The program DIFABS [25] and SHELXTL/PC program package [26] were used for computations. The hydrogen atoms of substituted pyridines were included on calculated positions by use of the HFIX utility [26]. In case of **1**, the *Flack* absolute structure parameter [26] was refined to 0.06(3). Split occupancies of 0.706(9) and 0.294(9) were refined for atoms of disordered *2picNO* molecule in case of **3**.

Table 5. Crystallographic data and processing parameters

Compound	**1**	**2**	**3**	**4**
Formula	$C_{12}H_{14}N_{14}O_2Zn_2$	$C_5H_6N_8Zn$	$C_6H_7CdN_7O$	$C_5H_6CdN_8$
Formula weight	517.15	243.54	305.50	290.58
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1$	P-1	P-1	$P2_1/n$
Cell parameter	$a = 610.6(2)$ pm	$a = 603.7(3)$ pm	$a = 626.6(3)$ pm	$a = 893.7(4)$ pm
	$b = 778.8(2)$ pm	$b = 700.8(4)$ pm	$b = 802.4(4)$ pm	$b = 812.9(3)$ pm
	$c = 2058.6(8)$ pm	$c = 1074.9(5)$ pm	$c = 1066.6(5)$ pm	$c = 1076.8(5)$ pm
	$\alpha = 90°$	$\alpha = 89.58(3)°$	$\alpha = 68.50(3)°$	$\alpha = 90°$
	$\beta = 97.57(3)°$	$\beta = 87.06(3)°$	$\beta = 86.03(3)°$	$\beta = 109.11(3)°$
	$\gamma = 90°$	$\gamma = 67.09(3)°$	$\gamma = 66.06(3)°$	$\gamma = 90°$
V/pm^3	$970.4(6) \cdot 10^6$	$418.3(4) \cdot 10^6$	$480.1(4) \cdot 10^6$	$876.5(6) \cdot 10^6$
Z	2	2	2	4
μ(MoKα)/mm^{-1}	2.516	2.906	2.259	2.464
D_{calc}/Mg $\cdot$ m^{-3}	1.770	1.934	2.113	2.202
Crystal size/mm	0.20 × 0.15 × 0.08	0.20 × 0.18 × 0.10	0.35 × 0.20 × 0.08	0.30 × 0.20 × 0.08
Theta range/°	2.80–27.00	3.16–25.11	2.94–27.99	3.02–25.00
Refl. collected	2805	1750	2312	1992
Indep. refl./R_{int}	2805/–	1497/0.0248	2306/0.0255	1545/0.0185
Parameters	273	128	202	128
GooF on F^2	1.092	1.039	1.091	1.190
$R1/wR2$ [$I > 2\sigma(I)$]	0.0418/0.0991	0.0239/0.0637	0.0374/0.0878	0.0302/0.0734
$R1/wR2$ (all data)	0.0504/0.1065	0.0246/0.0645	0.0445/0.0933	0.0327/0.0749
Residuals (e/Å^3)	0.533/−0.738	0.404/−0.431	0.724/−1.785	0.792/−1.146

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publication Nos. CCDC-197164–CCDC-197167 for **1**–**4**, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (FAX: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk

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References

[1] Batten SR, Robson R (1998) Angew Chem, Int Ed Engl **37**: 1460; Blake AJ, Champness NR, Hubberstey P, Li W-S, Schröder M, Withersby MA (1999) Coord Chem Rev **183**: 117
[2] James L (2003) Chem Soc Rev **32**: 276
[3] Withersby MA, Blake AJ, Champness NR, Hubberstey P, Li W-S, Schröder M (1997) Angew Chem **109**: 2421; Withersby MA, Blake AJ, Champness NR, Hubberstey P, Li W-S, Schröder M (1997) Angew Chem, Int Ed Engl **36**: 2327
[4] Tong M-L, Yu X-L, Chen X-M (1998) J Chem Soc Dalton Trans 5
[5] Fujita M, Kwon YJ, Washizu S, Ogura K (1994) J Am Chem Soc **116**: 1151
[6] McGillivary LR, Subramamian S, Zaworotka MJ (1994) J Chem Soc Chem Commun 1325
[7] Mautner FA, Abu-Youssef MAM, Goher MAS (1997) Polyhedron **16**: 235
[8] Agrell I (1970) Acta Chem Scand **24**: 3575; Agrell I (1967) Acta Chem Scand **21**: 2647
[9] Clegg W, Krischner H, Saracoglu AI, Sheldrick GM (1982) Z Kristallogr **161**: 307
[10] Krischner H, Kratky C, Maier HE (1982) Z Kristallogr **161**: 225
[11] Mondal A, Saha MK, Mitra S, Gramlich V (2000) J Chem Soc Dalton Trans 3218
[12] Chen H-J, Chen X-M (2002) Inorg Chim Acta **329**: 13
[13] Goher MAS, Mautner FA, Abu-Youssef MAM, Hafez AK, Badr AM-A (2002) J Chem Soc Dalton Trans 3309
[14] Goher MAS, Mautner FA, Hafez AK, Abu-Youssef MAM, Gspan C, Badr AM-A (2003) Polyhedron **22**: 975
[15] Goher MAS, Mautner FA, Abu-Youssef MAM, Hafez AK, Badr AM-A, Gspan C (2003) Polyhedron **22**: 3137
[16] Mautner FA, Gspan C, Goher MAS, Abu-Youssef MAM (2003) Monatsh Chem **134**: 1311
[17] Goher MAS, Mautner FA (1995) Polyhedron **14**: 1751
[18] Agrell I (1971) Acta Chem Scand **25**: 2965; Goher MAS (1990) Acta Chim Hung **127**: 213
[19] Mautner FA, Kratky C (1988) Cryst Res Technol **23**: 1477
[20] Mautner FA, Krischner H, Kratky C (1987) Z Kristallogr **180**: 219
[21] Mautner FA, Krischner H, Kratky C (1988) Z Naturforsch **43B**: 253
[22] Mautner FA, Krischner H (1992) Monatsh Chem **123**: 325
[23] Gillespie RJ (1963) J Chem Soc 4679
[24] Wöhler L, Martin F (1914) Angew Chem **27**: 335; Wöhler L, Martin F (1917) Angew Chem **30**: 33
[25] Walker N, Stuart D (1983) Acta Crystallogr **A39**: 158
[26] *SHELXTL/PC 5.03 (PC-Version)* (1995) Siemens Analytical Instruments Division, Madison, WI