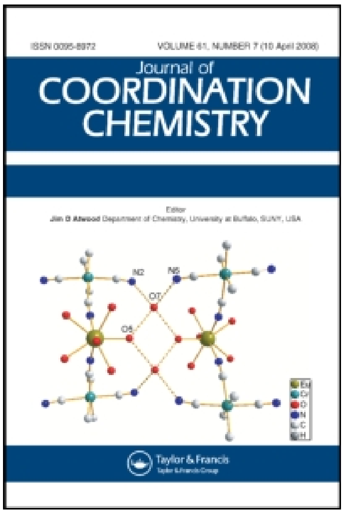

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Two new 1D cadmium(II) azido complexes: *catina*-Poly[di-$\mu_{1,1}$-azido(2,2'-bipyridyl)cadmium(II)] and a new polymorph of *catina*-Poly[di-$\mu_{1,1}$-azido (2-acetylpyridine)cadmium(II)]

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Two new cadmium(II) azido complexes, $[Cd(2,2'\text{-bipy})(N_3)_2]_n$ (**1**) and $[Cd(2\text{-acpy})(N_3)_2]_n$ (**2**) (2,2′-bipy = 2,2′-bipyridyl and 2-acpy = 2-acetylpyridine), have been synthesized and structurally characterized by single-crystal X-ray diffraction methods. The coordination environment of the central cadmium atom is distorted octahedral (MN_6) in **1** and (MN_5O) in **2**, with one-dimensional chains formed through Cd_2N_2 units and alternatively chelating N,N′-bipyridyl or N,O-2-acetylpyridine groups. The central Cd(II) ion is coordinated to two nitrogen atoms of a chelating bipyridyl group or one nitrogen atom and one acetyl oxygen of 2-acetylpyridine and four nitrogen atoms of four different end-on bridging ($\mu_{1,1}$-N_3) groups. Chains in the *c* direction in **1** are stabilized in *b* direction by π–π interactions involving the aromatic rings of bipyridyl ligands. IR and NMR spectra of the two complexes are reported.

Keywords: Cadmium(II); 2,2′-Bipyridyl; 2-Acetylpyridine; Azido complexes; IR and NMR spectra; X-ray structure

1. Introduction

The pursuit of high dimensional polymeric crystalline assemblies extending across a wide variety of organic/inorganic hybrid compounds has been motivated by interest in creating structures with new topologies, cavities and channels of potential use in adsorption, ion exchange, non-linear optical and magnetic materials [1, 2]. Polynuclear d^{10} metal complexes are attractive due to the fact that they exhibit intriguing structures and photoluminescent properties [3]. Investigations in this field have resulted in many kinds of materials with interesting structures using neutral organic ligands such as pyrazine, 4,4′- and 2,2′-bipyridine, 2,2′-bipyridylamine and other bidentate ligands [4–6].

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The versatile azide ligand can link metal ions in $\mu_{1,1}$- (end-on, EO), $\mu_{1,3}$- (end-to-end, EE), $\mu_{1,1,3}$-, $\mu_{1,1,1}$- or other modes, yielding various polynuclear, one-, two-, or three-dimensional species with specific topologies. Although several systems and topologies have been reported with this trend for Mn(II), Ni(II) and Cu(II), Cd(II) polymers are few in number [7–9]. It is noted that the explosive nature of metal azido complexes is dependent on the mode of bonding of bridged azides. Metal azido complexes have recently attracted a lot of interest as building blocks for construction of molecular-based materials (M(II) = Mn^{2+}, Zn^{2+}, Cd^{2+}) [10, 11].

We recently reported a number of Zn^{2+} and Cd^{2+} azido and thiocyanato coordination polymers with some pyridine derivatives showing different bridging modes and topologies [12–15]. We now extend this work to include the reaction of Cd^{2+} ions with 2,2′-bipyridyl in the presence of azide ions. We have also modified the reaction between cadmium(II) ions, 2-acetylpyridine (2-acpy) and azide ions to produce a complex with a 1 : 1 $Cd(N_3)_2$: 2-acpy ratio. Here we report the synthesis and structural characterization of these two complexes.

2. Experimental

2.1. *Materials and instrumentation*

C, H, N analyses were carried out using a Perkin-Elmer instrument and Cd^{2+} was determined using a Perkin-Elmer Analyst 300 AAS atomic absorption spectrometer. Infrared spectra were recorded on a Bruker IFS-125 FTIR spectrophotometer (KBr pellets). ^1H and ^{13}C NMR (DMSO-d_6) spectra were recorded on a Jeol JNM-ECA 500 MHz spectrometer. The ligands 2,2′-bipyridyl and 2-acetylpyridine purchased from Aldrich and other chemicals were of analytical grade quality and used as received.

2.2. *Synthesis*

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

2.2.1. [Cd(2,2′-bipy)(N_3)$_2$]$_n$ (1). To an aqueous solution (20 cm^3) of $3CdSO_4 \cdot 8H_2O$ (0.77 g, 1.0 mmol) a solution of 2,2′-bipyridyl (0.46 g, 3 mmol) in methanol (15 cm^3) was added, followed by dropwise addition of an aqueous solution of NaN_3 (0.65 g, 10 mmol), with continuous stirring. The turbid mixture was heated to boiling, filtered, boiled again, the final clear mixture allowed to cool gradually to room temperature and then placed in a refrigerator for several days. Colourless plates suitable for X-ray measurements were collected and dried in air (yield ~65%). Anal. Calcd (%): C, 34.06; H, 2.29; N, 31.78; Cd, 31.88. Found: C, 33.96; H, 2.21; N, 31.90; Cd, 31.69. IR (cm^{-1}) (vs = very strong; s = strong; ms = medium strong; w = weak; br = broad): 2056 vs, 2035 vs (ν_{as}-N_3), 1588 vs, 1560 ms, 1485 ms, 1471 ms, 1437 vs, 1334 s, 1314 ms, 1284 s (ν_s-N_3), 1174 s, 1161 s, 1043 s, 1014 s, 765 vs, 735 ms, 648 ms, 593 ms, 406 ms (bipy vibrations), 365 ms, 341 ms, 316 ms, 293 wm, 270 ms. ^1H-NMR (DMSO-d_6): δ 8.69 (d, 2H), 8.53 (d, 2H), 8.15 (t, 2H), 7.69 (t, 2H). ^{13}C-NMR (DMSO-d_6): δ 150.29, 149.62, 140.41, 126.45, 122.71.

2.2.2. [Cd(2-acpy)$(N_3)_2$]$_n$ (2). The complex was prepared by combining 15 cm^3 of an aqueous solution of NaN_3 (0.98 g, 15 mmol) with an aqueous solution of $3CdSO_4 \cdot 8H_2O$ (0.76 g, 1.0 mmol) and 2-acetylpyridine (0.48 g, 4 mmol) in 15 cm^3 of ethanol. The solution was heated for several minutes then allowed to stand at room temperature for several days; colourless crystals suitable for X-ray diffraction were collected and dried in air (yield ~65%). Anal. Calcd (%): C, 26.44; H, 2.22; N, 30.87; Cd, 35.35. Found: C, 26.40; H, 2.18; N, 31.05; Cd, 35.40. IR (cm^{-1}) 2100, 2050, 2035 vs (ν_{as}-N_3), 1670 vs (ν_{as}-C=O), 1590 s, 1569 ms, 1438 ms, 1418 ms, 1360 s, 1337 s, 1318 s, 1287 s (ν_s-N_3), 1247 ms, 1223 ms, 1164 ms, 1119 ms, 783 s, 653 wm, 639 ms, 613 ms, 594 ms, 407 w (pyridine vibrations), 318 wm, 294 wm, 271 m (M-L vibrations). ^{1}H-NMR (DMSO-d$_6$): δ 2.58 (s, 3H), 7.71 (m, 1H), 8.19 (m, 1H), 8.21 (d, 1H), 8.65 (d, 1H).

2.3. *X-ray crystallography*

All diffraction data were collected using a Siemens SMART CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). Crystals were cooled to 173(2) K. Full spheres of reciprocal space were scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm. Preliminary orientation matrices were obtained from the first frames using SMART [16]. The collected frames were integrated using preliminary orientation matrices, which were updated every 100 frames. Final cell parameters were obtained by refinement of the positions of reflections with $I > 10\sigma(I)$ after integration of all the frames using SAINT [16]. Data were empirically corrected for absorption and other effects using the SADABS [17] program. The structures were solved by direct methods and refined by full-matrix least-squares on all F^2 data using SHELXTL [18]. Non-H atoms were refined anisotropically, while hydrogen atoms were refined isotropically with the use of geometrical restrains. Crystallographic and refinement data are summarized in table 1. Selected bond distance and bond angles for complexes **1** and **2** are given in tables 2 and 3, respectively. Molecular graphics (figures 1–5) were prepared using Diamond [19]. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers CCDC 268933 and CCDC 258681 for **1** and **2**, respectively.

3. Results and discussion

Two new azide compounds [Cd(2,2′-bipy)$(N_3)_2$]$_n$ (**1**) and [Cd(2-acpy)$(N_3)_2$]$_n$ (**2**) (2,2′-bipy = 2,2′-bipyridyl and 2-acpy = 2-acetylpyridine) have been synthesized and isolated. Complexes are photoluminescent and light sensitive, and are 1D coordination polymers. Previously we reported a polymorph of **2** with the same stoichiometry but with a different structural motif (2D) [13a]. The present dimorph of [Cd(2-acpy)$(N_3)_2$]$_n$ was synthesized by a different route. Complexes **1** and **2** are insoluble in both non-polar (benzene, CCl_4) and polar solvents (H_2O, MeOH, EtOH, $CHCl_3$, acetone), indicating their polymeric natures. Both complexes are slightly soluble in DMSO.

Table 1. Crystallographic data and structure refinement for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{10}H_8CdN_8$	$C_7H_7CdN_7O$
Formula weight	352.64	317.60
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions	$a = 20.2435(3)$ Å $b = 9.4740(2)$ Å $c = 6.7045(2)$ Å $\beta = 107.330(1)°$	$a = 6.7816(1)$ Å $b = 8.4324(1)$ Å $c = 10.7426(1)$ Å $\alpha = 70.921(1)°$ $\beta = 72.026(1)°$ $\gamma = 67.145(1)°$
Volume	1227.46(5) Å^3	523.227(11) Å^3
Z	4	2
Density (calculated)	1.908 Mg m^{-3}	2.016 Mg m^{-3}
Absorption coefficient	1.778 mm^{-1}	2.077 mm^{-1}
$F(000)$	688	308
Crystal size	$0.08 \times 0.06 \times 0.04$ mm^3	$0.36 \times 0.32 \times 0.26$ mm^3
Theta range for data collection	2.11 to 32.59°	2.70 to 32.93°
Index ranges	$-30 \leq h \leq 30$, $-13 \leq k \leq 14$, $-9 \leq l \leq 8$	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-16 \leq l \leq 15$
Reflections collected	9171	9212
Independent reflections	2141 [R(int) = 0.0603]	3630 [R(int) = 0.0217]
Max. and min. transmission	0.932 and 0.871	0.614 and 0.522
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2141/0/91	3630/0/153
Goodness-of-fit on F^2	1.014	1.038
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0416$, $wR2 = 0.0899$	$R1 = 0.0211$, $wR2 = 0.0554$
R indices (all data)	$R1 = 0.0569$, $wR2 = 0.0973$	$R1 = 0.0219$, $wR2 = 0.0560$
Largest diff. peak and hole	1.793 and −1.388 e Å^{-3}	2.001 and −0.745 e Å^{-3}

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

Cd(1)–N(1A)	2.312(3)	Cd(1)–N(1A)^{ii}	2.422(3)
Cd(1)–N(1A)^{i}	2.312(3)	Cd(1)–N(1A)^{iii}	2.422(3)
Cd(1)–N(1)	2.364(3)	N(1A)–N(2A)	1.208(4)
Cd(1)–N(1)^{i}	2.364(3)	N(2A)–N(3A)	1.159(5)
N(1A)^{i}–Cd(1)–N(1A)	107.38(17)	N(1A)^{i}–Cd(1)–N(1A)^{iii}	74.36(11)
N(1A)^{i}–Cd(1)–N(1)^{i}	95.15(10)	N(1A)–Cd(1)–N(1A)^{iii}	95.32(10)
N(1A)–Cd(1)–N(1)^{i}	151.83(11)	N(1)^{i}–Cd(1)–N(1A)^{iii}	107.14(11)
N(1A)^{i}–Cd(1)–N(1)	151.83(11)	N(1)–Cd(1)–N(1A)^{iii}	87.15(9)
N(1A)–Cd(1)–N(1)	95.15(10)	N(1A)^{ii}–Cd(1)–N(1A)^{iii}	162.82(15)
N(1)^{i}–Cd(1)–N(1)	69.83(13)	N(2A)–N(1A)–Cd(1)	121.2(2)
N(1A)^{i}–Cd(1)–N(1A)^{ii}	95.32(10)	N(2A)–N(1A)–Cd(1)^{ii}	132.8(2)
N(1A)–Cd(1)–N(1A)^{ii}	74.36(11)	Cd(1)–N(1A)–Cd(1)^{ii}	105.65(11)
N(1)^{i}–Cd(1)–N(1A)^{ii}	87.15(9)	N(3A)–N(2A)–N(1A)	179.2(3)
N(1)–Cd(1)–N(1A)^{ii}	107.14(11)		

Symmetry transformations used to generate equivalent atoms are (i): $-x, y, -z+3/2$; (ii): $-x, -y+2, -z+2$; (iii): $x, -y+2, z-1/2$.

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

Cd(1)–N(1A)	2.2473(16)	N(1A)–N(2A)	1.202(2)
Cd(1)–N(1B)	2.2958(15)	N(1A)–Cd(1)^{ii}	2.4280(16)
Cd(1)–N(1)	2.3194(15)	N(2A)–N(3A)	1.146(3)
Cd(1)–N(1B)^{i}	2.3823(15)	N(1B)–N(2B)	1.209(2)
Cd(1)–O(9)	2.3993(14)	N(1B)–Cd(1)^{i}	2.3823(15)
Cd(1)–N(1A)^{ii}	2.4280(16)	N(2B)–N(3B)	1.149(3)
N(1A)–Cd(1)–N(1B)	100.22(6)	N(1)–Cd(1)–N(1A)^{ii}	82.69(5)
N(1A)–Cd(1)–N(1)	156.27(6)	N(1B)^{i}–Cd(1)–N(1A)^{ii}	170.70(5)
N(1B)–Cd(1)–N(1)	97.19(6)	O(9)–Cd(1)–N(1A)^{ii}	87.11(5)
N(1A)–Cd(1)–N(1B)^{i}	107.33(6)		
N(1B)–Cd(1)–N(1B)^{i}	80.34(6)	N(2A)–N(1A)–Cd(1)^{ii}	118.52(13)
N(1)–Cd(1)–N(1B)^{i}	91.35(5)	Cd(1)–N(1A)–Cd(1)^{ii}	103.20(6)
N(1A)–Cd(1)–O(9)	97.22(6)	N(3A)–N(2A)–N(1A)	177.5(2)
N(1B)–Cd(1)–O(9)	159.43(5)	N(2B)–N(1B)–Cd(1)	118.56(13)
N(1)–Cd(1)–O(9)	69.67(5)	N(2B)–N(1B)–Cd(1)^{i}	114.68(12)
N(1B)^{i}–Cd(1)–O(9)	84.12(5)	Cd(1)–N(1B)–Cd(1)^{i}	99.66(6)
N(1A)–Cd(1)–N(1A)^{ii}	76.80(6)	N(3B)–N(2B)–N(1B)	178.5(2)
N(1B)–Cd(1)–N(1A)^{ii}	107.40(6)		

Symmetry transformations used to generate equivalent atoms are (i): $-x$, $-y+2$, $-z+1$; (ii): $-x+1$, $-y+2$, $-z+1$.

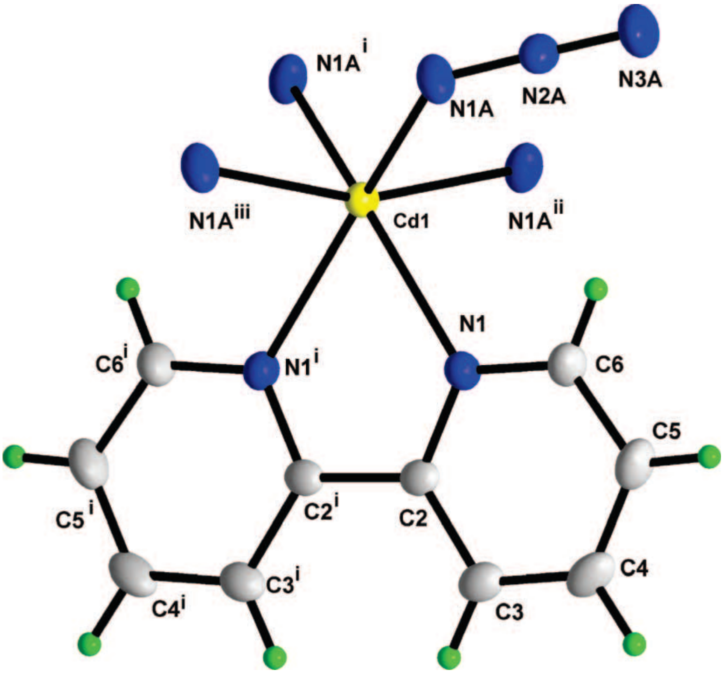

Figure 1. Numbering scheme for $[Cd(2,2'\text{-bipy})(N_3)_2]_n$, **1**, with atomic displacement ellipsoids drawn at the 50% probability level. For symmetry codes see table 2.

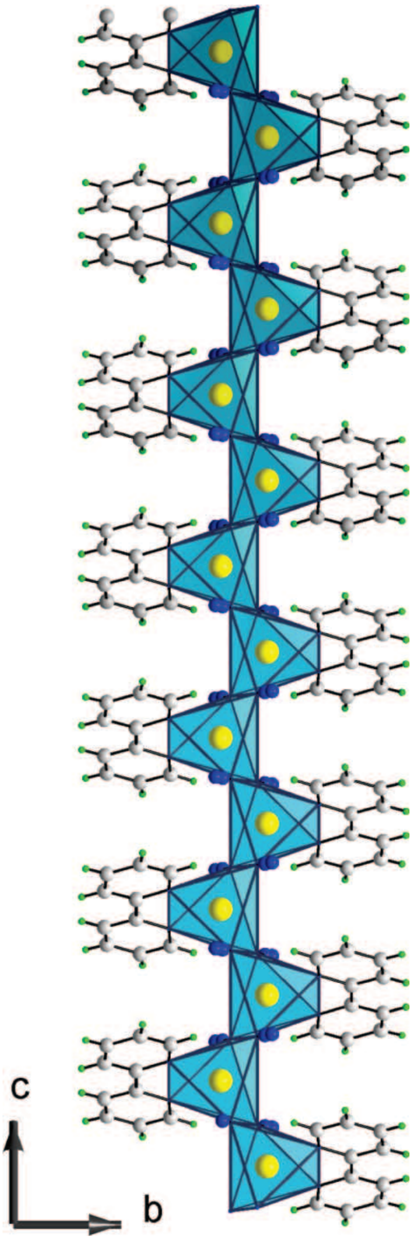

Figure 2. The 1D chain formed in the $[Cd(2,2'\text{-bipy})(N_3)_2]_n$ complex.

3.1. *Structures*

3.1.1. $[Cd(2,2'\text{-bipy})(N_3)_2]_n$ (1). The structure of **1** is illustrated in figure 1. It consists of 1D, neutral zigzag chains along the *c* axis (figure 2) containing Cd_2N_2 units. Cd atoms are octahedrally coordinated by four EO (μ-1,1) azide ions and one bidentate 2,2′-bipy group. The octahedral geometry around Cd(II) is highly distorted, with an

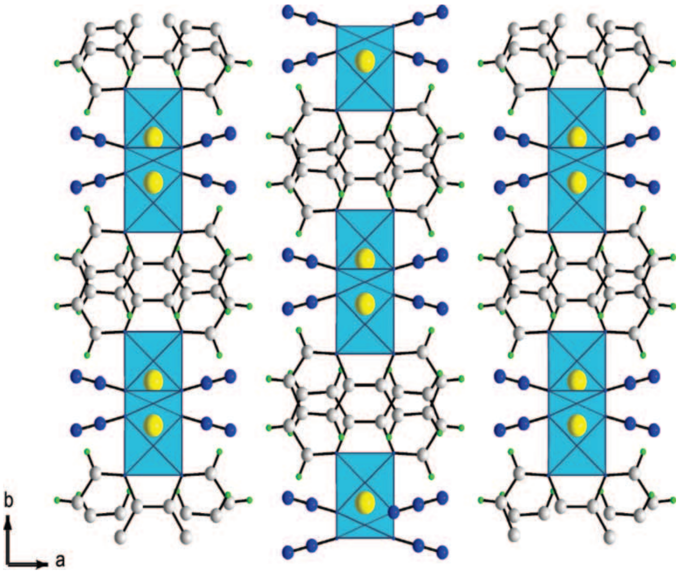

Figure 3. Projection of **1** structure along the *c* axis. The chains are stabilized in the *b* direction by π–π interactions.

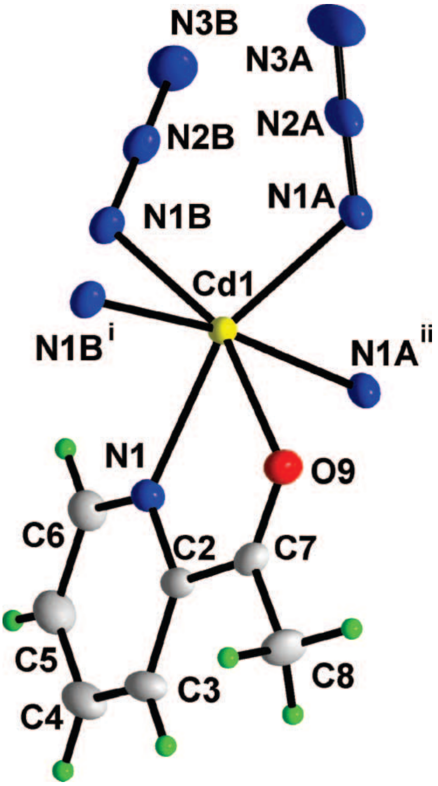

Figure 4. Numbering scheme for $[Cd(2\text{-acpy})(N_3)_2\}_n$, **2**, with atomic displacement ellipsoids drawn at the 50% probability level. For symmetry codes see table 3.

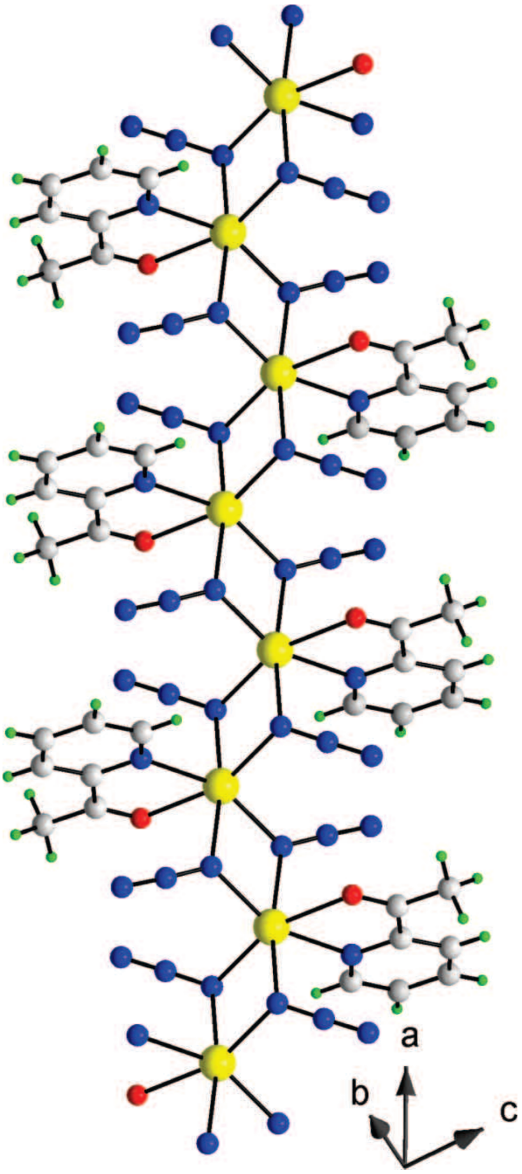

Figure 5. A 1D chain of [Cd(2-acpy)$(N_3)_2\}_n$, **2**, propagating in the *a* direction.

acute bipyridyl bite (N1^i–Cd–N1, 69.8(1)°) and a *transoid* N1(bipy)–Cd–N1A^i(azido) angle of 151.8(1)°. Octahedra share two edges with two adjacent EO azido mediated Cd octahedra. The coordinated nitrogens of the EO bridging azide groups have Cd–N distances of 2.312(3) to 2.422(3) Å, while the two Cd–N (bipy) bonds are identical (2.364(3) Å). Cd–N (EO-azide) bond lengths are in the same range as in similar Cd complexes with different hetero-nitrogen donors [20, 21]. Azide groups are asymmetric with N–N bond distances of 1.208 and 1.159 Å, respectively. The structure is unique in that it contains four EO azido bridges and is unlike that of

[Zn(bipy)$(N_3)_2$]$_n$ [22]. The structure as shown in figure 3 is stabilized through π–π interactions between bipyridyl groups in parallel chains with interplanar distances of 3.29(1) Å.

3.1.2. [Cd(2-acpy)$(N_3)_2$]$_n$ (2).

The principle structural features of complex **2** are illustrated in figure 4. Each Cd(II) centre is six-coordinated by four azido groups [Cd–N distances ranging from 2.2473(16) to 2.4280(16) Å], a hetero N atom of 2-acpy [Cd–N = 2.3194(15) Å] and the oxygen atom of the same chelating μ-N,O-2-acpy ligand [Cd–O = 2.3993(14) Å]. The four azido groups act as EO bridges [N(1A)–N(2A)–N(3A)] linking the Cd(II) centre to form four-membered Cd_2N_2 rings connected together in a 1D chain (figure 5). Chelating 2-acpy ligands are located on alternate sides of this chain in a zigzag manner along the *a* axis. Similar 1D chain complexes [Cd(bipy)Cl_2]$_n$ and [Cd(1,10-phenanthroline)Cl_2]$_n$ consisting of a zigzag Cd_2Cl_2 subunit and chelating bipyridine or 1,10-phenanthroline ligands on alternate sides [5]. The azido groups are not symmetric [N(1A)–N(2A) 1.202(2), N(2A)–N(3A) 1.146(3) Å and N(1B)–N(2B) 1.209(2), N(2B)–N(3B) 1.149(3) Å], but are close to linear [N(3A)–N(2A)–N(1A) 177.5(2), N(3B)–N(2B)–N(1B) 178.5(2)°]. We recently reported another polymorph of complex **2** with a 2D structure generated by alternating bridging di-$\mu_{1,3}$-azido and $\mu_{1,1}$-azido groups [13a]. This structure also contains a chelating 2-acpy ligand alternating on the sides of the 2D motif.

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