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Synthesis and crystal structure of three new 2D polymeric cadmium(II) complexes of some pyridine derivatives with different cadmium(II)–azide topologies

Mohamed A. S. Goher,*[a] Franz A. Mautner,[b] Morsy A. M. Abu-Youssef,[a] Afaf K. Hafez[a] and Ahmed M.-A. Badr[a]

[a] *Departement of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426 Ibrahimia, Alexandria, Egypt*

[b] *Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Graz 8010, Austria*

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Three new polymeric complexes $[Cd(2\text{-}Acpy)(N_3)_2]_n$ **1**, $[Cd(4\text{-}Acpy)_2(N_3)_2]_n$ **2** and $[Cd_3(4\text{-}Brpy)_4(N_3)_6]_n$ **3** (2-Acpy = 2-acetylpyridine, 4-Acpy = 4-acetylpyridine, and 4-Brpy = 4-bromopyridine) have been synthesized and characterized by single crystal X-ray diffraction. The coordination environment of the cadmium atom in all the complexes is distorted octahedral with two-dimensional polynuclear layers. The cadmium atoms are linked by both μ-1,1 and μ-1,3 in **1**, by only μ-1,3 in **2** and by μ-1,1 and μ-1,1,3 azide bridges in **3** giving different cadmium(II)–azide topologies.

Introduction

The area of coordination polymers has been motivated by the ability of coordination polymers to provide a facile approach to the controlled assembly of one-, two-, or three-dimensional extended networks. The chemistry of these polymers is of considerable interest for the potential application of them as catalysts, molecular sieves and as ion exchangers.[1–3] Investigations in this direction have led to many materials of interesting structure, with neutral organic ligands like pyrazine and 4,4′-bipyridine.

Charged ligands like azide are also used to bridge metal centers, which give complexes of anomalous architectures with important physical properties such as supramolecular chemistry[4] and molecular magnetism.[5] The azide[6,7] anion is a versatile ligand that can bridge metal centers either end-to-end (μ-1,3) or end-on (μ-1,1), both possibilities being structurally characterized for transition metal complexes.[8,9] When the azido group acts as a bridging ligand with an end-on coordination mode the resulting binuclear complexes usually show ferromagnetic behavior, whereas end-to-end coordination results in antiferromagnetic behavior.[9] Although systematic azido complexes of manganese(II),[10] nickel(II),[11] and copper(II)[12] with pyridine derivatives and other ligands have been synthesized and characterized, the corresponding cadmium(II) complexes are still very few.[13–18] These cadmium complexes have been found to contain either μ-1,3 (end-to-end), μ-1,1 (end-on) or μ-1,1,3 bridging azides. This paper elucidates the synthesis, spectral and structural studies of three azido-bridged complexes of cadmium(II) with 2-acetylpyridine (2-Acpy) **1**, 4-acetylpyridine (4-Acpy) **2** and 4-bromopyridine (4-Brpy) **3**. Although these three complexes have two-dimensional structures the topologies of the cadmium(II)–azide layer are different. The azido-bridged complex **3** is the first example of cadmium(II) chains containing both μ-1,1 and μ-1,1,3 bridging modes of azide ligands.

Experimental

Physical measurements and materials

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Infrared spectra were recorded on a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets. 2-Acetylpyridine, 4-acetylpyridine and 4-bromopyridine were purchased from Aldrich company and other chemicals were of analytical grade quality and used as received.

Preparation of $[Cd(2\text{-}Acpy)(N_3)_2]_n$ (1)

This complex was prepared by mixing $3CdSO_4\cdot 8H_2O$ (0.5 g, 1.95 mmol) in water (15 ml) with 2-Acpy (0.5 ml, 4.46 mmol) in 10 ml ethanol. An aqueous solution (5 ml) of NaN_3 (0.325 g, 5 mmol) was added dropwise with continuous stirring. The final mixture was allowed to stand for several days in a refrigerator to deposit colorless crystals of the complex suitable for X-ray measurements. Yield, *ca.* 65%. Found % (calc.): C, 38.2(38.32); H, 3.5(3.45); N, 25.6(25.53); Cd, 25.8(25.52).

Preparation of $[Cd(4\text{-}Acpy)_2(N_3)_2]_n$ (2)

Complex **2** was synthesized by mixing 4-acetylpyridine (4 ml, 17.84 mmol) in 10 ml methanol with $3CdSO_4\cdot 8H_2O$ (0.55 g, 2.145 mmol) in 40 ml water, followed by dropwise addition of an aqueous solution (5 ml) of NaN_3 (1.0 g, 15.38 mmol) with constant stirring. The final mixture was kept in a refrigerator for several weeks until good quality yellow crystals of the complex were obtained. Yield, 55%. Found % (calc.): C, 26.2(26.36); H, 2.4(2.21); N, 31.1(30.87); Cd, 35.6(35.41).

Preparation of $[Cd_3(4\text{-}Brpy)_4(N_3)_6]_n$ (3)

Complex **3** was synthesized by addition of an ethanol solution (10 ml) of 4-bromopyridine (1.00 g, 6.33 mmol) to a 20 ml aqueous solution of $3CdSO_4\cdot 8H_2O$ (0.5 g, 1.95 mmol) followed by dropwise addition of a 5 ml aqueous solution of NaN_3 (0.325 g, 5 mmol). Colorless crystals were obtained by allowing the final mixture to stand over several days in a refrigerator. Yield, *ca.* 60%. Found % (calc.): C, 19.5(19.65); H, 1.4(1.31); N, 25.5(25.23); Cd, 27.5(27.62).

Crystal structure determination

The X-ray single-crystal data for $[Cd(2\text{-}Acpy)(N_3)_2]_n$ **1**, $[Cd(4\text{-}Acpy)_2(N_3)_2]_n$ **2** and $[Cd_3(4\text{-}Brpy)_4(N_3)_6]_n$ **3** were collected on a modified STOE four circle diffractometer. The crystallographic data, conditions retained for the intensity data

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Table 1 Crystal data and structure refinement for $[Cd(2\text{-}Acpy)(N_3)_2]_n$ **1**, $[Cd(4\text{-}Acpy)_2(N_3)_2]_n$ **2** and $[Cd_3(4\text{-}Brpy)_4(N_3)_6]_n$ **3**

Compound	1	2	3
Formula	$C_7H_7CdN_7O$	$C_{14}H_{14}CdN_8O_2$	$C_{20}H_{16}Br_4Cd_3N_{22}$
Formula weight	317.60	438.73	1221.39
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$
a/Å	9.107(4)	8.690(3)	6.814(2)
b/Å	13.696(5)	8.522(3)	9.367(2)
c/Å	9.310(4)	11.216(5)	13.274(5)
a/°	90	90	82.08(2)
β/°	114.11(3)	94.81(3)	81.58(2)
γ/°	90	90	88.91(2)
V/Å^3	1059.9(8)	827.7(6)	830.1(4)
Z	4	2	1
T/K	90(2)	95(2)	100(2)
μ(MoKα)/mm^{-1}	2.051	1.346	6.772
ρ_{calc}/Mg m^{-3}	1.990	1.760	2.443
R^a	0.0435	0.0431	0.0375
$wR2^b$	0.1013	0.1069	0.0783

^{a} $R = \Sigma(F_o - F_c)/\Sigma F_o$. ^{b} $wR2 = \{\Sigma[w((F_o^2) - (F_c^2))^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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

Cd(1) ··· Cd(1a)	3.561(1)	Cd(1) ··· Cd(1b)	6.080(2)
Cd(1)–N(11)	2.262(6)	Cd(1)–N(21)	2.275(6)
Cd(1)–N(1)	2.322(6)	Cd(1)–N(11a)	2.330(5)
Cd(1)–N(23b)	2.377(6)	Cd(1)–O(1)	2.426(4)
N(11)–N(12)	1.213(8)	N(12)–N(13)	1.150(8)
N(21)–N(22)	1.176(8)	N(22)–N(23)	1.177(7)
N(1) ··· O(1)	2.695(7)		
N(11)–Cd(1)–N(21)	106.3(2)	N(11)–Cd(1)–N(1)	163.8(2)
N(21)–Cd(1)–N(1)	89.5(2)	N(11)–Cd(1)–N(11a)	78.3(2)
N(21)–Cd(1)–N(11a)	97.2(2)	N(1)–Cd(1)–N(11a)	96.2(2)
N(11)–Cd(1)–N(23b)	89.8(2)	N(21)–Cd(1)–N(23b)	90.9(2)
N(1)–Cd(1)–N(23b)	93.9(2)	N(11a)–Cd(1)–N(23b)	167.1(2)
N(11)–Cd(1)–O(1)	96.3(2)	N(21)–Cd(1)–O(1)	154.8(2)
N(1)–Cd(1)–O(1)	69.1(2)	N(11a)–Cd(1)–O(1)	98.2(2)
N(23b)–Cd(1)–O(1)	78.0(2)	N(12)–N(11)–Cd(1)	123.0(4)
N(12)–N(11)–Cd(1a)	127.5(4)	Cd(1)–N(11)–Cd(1a)	101.7(2)
N(13)–N(12)–N(11)	178.3(7)	N(22)–N(21)–Cd(1)	125.8(5)
N(23)–N(22)–N(21)	177.8(7)	N(22)–N(23)–Cd(1c)	113.7(4)

Symmetry codes: (a) $-x, -y + 1, -z$; (b) $x + 1/2, -y + 1/2, z$; (c) $x - 1/2, -y + 1/2, z$.

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

Cd(1) ··· Cd(1b)	6.086(2)	Cd(1)–N(13b)	2.323(5)
Cd(1)–N(11)	2.326(4)	Cd(1)–N(1)	2.351(4)
N(11)–N(12)	1.184(6)	N(12)–N(13)	1.183(7)
N(13c)–Cd(1)–N(11)	90.4(2)	N(11)–Cd(1)–N(1a)	91.6(2)
N(13b)–Cd(1)–N(1)	92.4(2)	N(12)–N(11)–Cd(1)	120.5(3)
N(13)–N(12)–N(11)	176.7(5)	N(12)–N(13)–Cd(1d)	149.0(4)

Symmetry codes: (a) $-x, -y, -z + 1$; (b) $x - 1/2, -y + 1/2, z$; (c) $-x + 1/2, y - 1/2, -z + 1$; (d) $-x + 1/2, y + 1/2, -z + 1$.

collection, and some features of the structure refinement are listed in Table 1. Graphite-monochromatized Mo-Kα radiation (λ = 0.71069 Å) with the ω-scan technique was used to collect the data sets. Corrections were applied for Lorentz-polarization effects, intensity decay and for absorption. 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. The program DIFABS[19] and the SHELXTL/PC program package[20] were used for computations. Selected bond parameters are given in Tables 2, 3 and 4 respectively.

CCDC reference numbers 180362–180364.

See http://www.rsc.org/suppdata/dt/b2/b202007f/ for crystallographic data in CIF or other electronic format.

Results and discussion

IR spectra

The substantial shift of the carbonyl stretching band from 1700 cm^{-1} in the spectrum of 2-Acpy to 1671 cm^{-1} in complex **1**, compared to the constant position of the corresponding band in 4-Acpy and its cadmium complex, suggests that 2-Acpy behaves as an N,O-bidentate ligand in complex **1**. Complex **2** shows a very strong band at 2037 cm^{-1}, due to υ_{asym} (N_3), but no band in the range 1275–1340 cm^{-1} could be assigned to υ_{sym} (N_3), suggesting the existence of symmetrical azido ligands of the μ-1,3 bridging type. Complexes **1** and **3** exhibit at least two bands in the range of 2035–2100 cm^{-1}, in addition to the medium to strong absorption bands in the region 1275–1340 cm^{-1}; a result which is suggestive of the existence of different modes of bridging azides.

Crystal structures

Fig. 1 illustrates the principle structural features of complex **1**, selected bond distances and bond angles are collected in Table 2. Each octahedral cadmium atom is coordinated by a

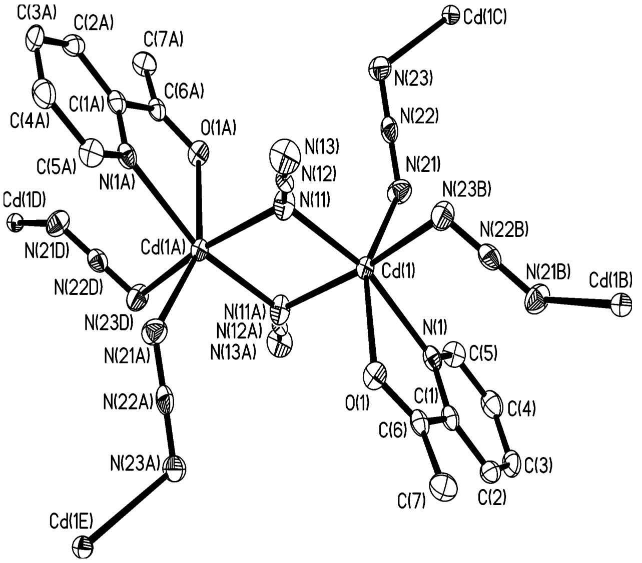

Fig. 1 Perspective view with atom labeling scheme of $[Cd(2\text{-}Acpy)(N_3)_2]_n$ **1**.

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

Cd(1) ··· Cd(2)	4.247(1)	Cd(1) ··· Cd(2b)	5.718(1)
Cd(2) ··· Cd(2b)	3.705(1)	Cd(1)–N(1)	2.341(6)
Cd(1)–N(31)	2.319(5)	Cd(1)–N(21)	2.339(5)
Cd(2)–N(21)	2.278(5)	Cd(2)–N(2)	2.322(6)
Cd(2)–N(11b)	2.329(5)	Cd(2)–N(33b)	2.330(5)
Cd(2)–N(11)	2.359(5)	N(33)–Cd(2d)	2.585(5)
N(11)–N(12)	1.195(8)	N(12)–N(13)	1.161(9)
N(21)–N(22)	1.217(8)	N(22)–N(23)	1.152(8)
N(31)–N(32)	1.152(8)	N(32)–N(33)	1.190(8)
N(31)–Cd(1)–N(21)	91.4(2)	N(31)–Cd(1)–N(1a)	94.0(2)
N(21)–Cd(1)–N(1)	95.6(2)	N(21)–Cd(2)–N(2)	98.2(2)
N(21)–Cd(2)–N(11b)	94.3(2)	N(2)–Cd(2)–N(11b)	164.1(2)
N(21)–Cd(2)–N(33b)	154.8(2)	N(2)–Cd(2)–N(33b)	84.9(2)
N(11b)–Cd(2)–N(33b)	88.0(2)	N(21)–Cd(2)–N(11)	108.1(2)
N(2)–Cd(2)–N(11)	91.1(2)	N(11b)–Cd(2)–N(11)	75.6(2)
N(33b)–Cd(2)–N(11)	96.8(2)	N(21)–Cd(2)–N(33e)	81.9(2)
N(2)–Cd(2)–N(33e)	80.1(2)	N(11b)–Cd(2)–N(33e)	111.6(2)
N(33b)–Cd(2)–N(33e)	74.0(2)	N(11)–Cd(2)–N(33e)	167.7(2)
N(12)–N(11)–Cd(2b)	123.3(4)	N(12)–N(11)–Cd(2)	121.9(4)
Cd(2b)–N(11)–Cd(2)	104.4(2)	N(13)–N(12)–N(11)	179.1(7)
N(22)–N(21)–Cd(2)	114.8(4)	N(22)–N(21)–Cd(1)	111.1(4)
Cd(2)–N(21)–Cd(1)	133.8(3)	N(23)–N(22)–N(21)	179.0(7)
N(32)–N(31)–Cd(1)	140.0(5)	N(31)–N(32)–N(33)	177.2(6)
N(32)–N(33)–Cd(2b)	120.5(4)	N(32)–N(33)–Cd(2d)	113.9(4)
Cd(2b)–N(33)–Cd(2d)	106.0(2)		

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

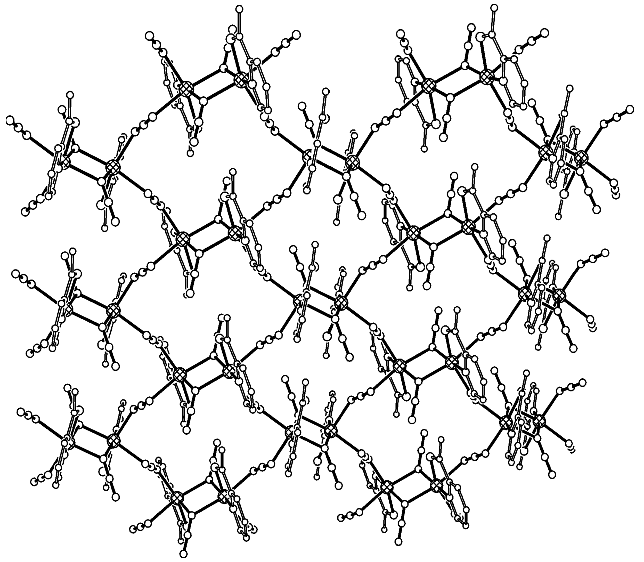

Fig. 2 View of a layer of the 2-D system $[Cd\ (2\text{-}Acpy)(N_3)_2]_n$ **1**. The layers are oriented parallel to the *ab*-plane of unit cell.

bidentate N,O-bridging 2-acetylpyridine ligand, and links another cadmium atom by double μ-1,1 azido bridges to form Cd_2N_2 dimeric units. Each unit is linked to another four units by four μ-1,3 azido ligands giving 2D polymeric chains (Fig. 2). The deviation of the 2-acetylpyridine ring is less than 0.005 Å (N(1)–C(5), C(6) = 0.06 Å; C(7) = 0.10 Å, and O(1) = 0.25 Å). The Cd(1)–N(21)···N(23)–Cd(1b) torsion angle is 156.6°, the Cd(1) ··· Cd(1b) distances are 3.561(1) and 6.080(2) Å. These values are very close to the corresponding values of 3.63(1) and 6.25(2) Å, respectively, found in the structure of $[Cd(dmen)(N_3)_2]_n$ (dmen = *N*,*N*-dimethylethylenediamine) also containing μ-1,1, and μ-1,3 azide bridges.[17] Similar topology with an alternating sequence of double μ-1,1 followed by double μ-1,3 bridging azido groups has been observed in the structures of $[Mn(N_3)_2(Etnic)_2]_n$ (Etnic = ethylnicotinate)[21] and *cis*-$[Mn(2,2'\text{-}bipy)(N_3)_2]_n$ (2,2′-bipy = 2,2′-bipyridine),[22] except that the former 2D complex contains two *trans* monodentate ethylnicotinate ligands and the latter has a one-dimensional structure.

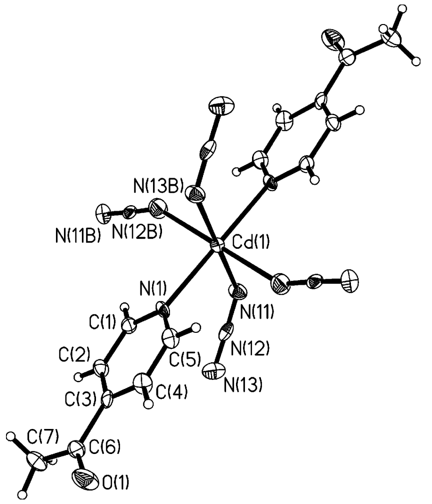

Fig. 3 Molecular structure and atom labelling scheme of $[Cd(4\text{-}Acpy)_2(N_3)_2]_n$ **2**.

The atom labeling scheme for complex **2** is shown in Fig. 3. Selected structural data are gathered in Table 3. The structure consists of an extended 2D layer of octahedrally coordinated centrosymmetric cadmium atoms, bridged by means of μ-1,3 azide ligands. Each cadmium atom has two 4-acetylpyridine ligands in *trans* arrangement and four azide ligands in the equatorial plane. The axial Cd–N(1) bond distance is 2.351(4) Å whereas the slightly shorter Cd–N(azide) bond lengths are Cd–N(11) 2.326(4) Å and Cd–N(13b) 2.323(5) Å. Each of the four azide ligands acts as a μ-1,3 bridge with each one of the neighbouring cadmium atoms giving an extended two-dimensional layer (Fig. 4). The bond angles Cd(1)–N(11)–N(12) and Cd(1d)–N(13)–N(12) take the values 120.5(3)° and 149.0(4)°, which lie in the normal M–N–N range found for μ-1,3 bridges within manganese, nickel or copper polynuclear complexes.[10–12] The torsion angles are Cd(1)–N(13b)–N(11b)–Cd(1b) = 91.5°, C(2)–C(3)–C(6)–C(7) = −4.6°, and C(2)–C(3)–C(6)–O(1) = 174.6°. The Cd(1) ··· Cd(1b) distance of 6.086(2) Å is very similar to the corresponding value given for complex **1**. Complex **2** is isostructural with that of $[Mn(4\text{-}Acpy)_2(N_3)_2]_n$[23] with a $Mn–N_3–Mn$ torsion angle of 98.1°.

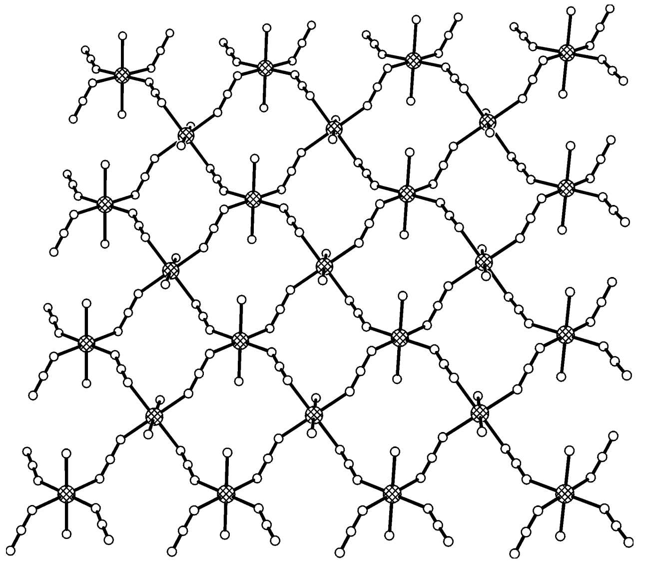

Fig. 4 Cd–N-sublattice of $[Cd(4\text{-}Acpy)_2(N_3)_2]_n$ **2**. Each Cd(II) center is connectd by four single *EE*-azido bridges to form sheets of polyhedra oriented normal to the *c*-axis of the unit cell.

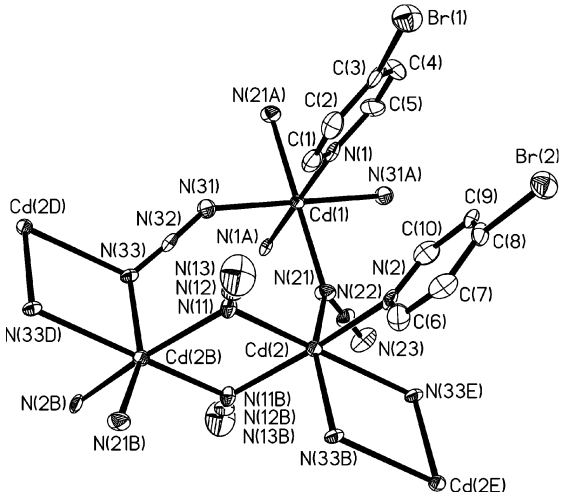

Fig. 5 Molecular structure and atom labeling scheme of $[Cd_3(N_3)_6(4\text{-}Brpy)_4]_n$ **3**.

The labeled structure for complex **3** is shown in Fig. 5, and selected bond distances and bond angles are listed in Table 4. In this structure, the Cd(1) atom which is located at the inversion center of the unit cell, is in a distorted octahedral environment with the coordination of two nitrogen atoms (N1, N1a) of monodentate 4-Brpy ligands, two nitrogen atoms (N21, N21a) of two different μ-1,1 azido bridges and the other two nitrogen atoms (N31, N31a) of two different μ-1,1,3 azido bridges. The Cd(2) atoms are also pseudo-octahedrally coordinated by double μ-1,1 azido bridges (N11, N11b) which are further linked to neighbors by double μ-1,1,3 azido bridges (N33b, N33e); both double bridges form dimeric subunits. The two other sites are occupied by nitrogen atoms (N2) from 4-Brpy and nitrogen atoms (N21) of μ-1,1 azido bridges. The 2D polymeric sheets of complex **3** are presented in Fig. 6. The Cd ··· Cd separation is 3.705(1) Å for the Cd_2N_2 units and the long Cd ··· Cd distance is 5.718(1) Å. Complex **3** is the first example of a cadmium(II)–azido compound that contains both μ-1,1 and μ-1,1,3 bridging azide ligands.

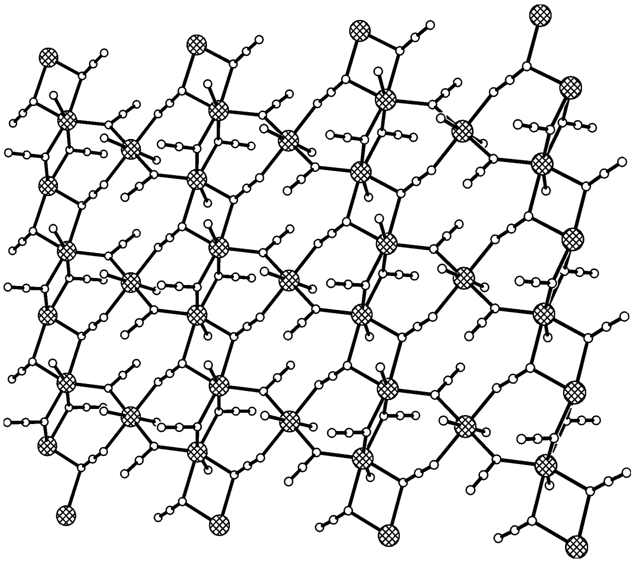

Fig. 6 $[Cd_3(N_3)_6(4\text{-}Brpy)_4]_n$ **3**. The Cd–N-sublattice has a layer system with di-, tri- and tetra-nuclear subunits formed by the μ(1,1,3)- and μ(1,1)-azido bridges.

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