Available online at www.sciencedirect.com
SCIENCE DIRECT®
PERGAMON
Polyhedron 22 (2003) 3137–3143
POLYHEDRON
www.elsevier.com/locate/poly

Structural characterization of one-, two-, and three-dimensional polymeric complexes assembled by cadmium(II) pseudohalides and some pyridine ligands via covalent bonds and hydrogen bonds

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

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

Received 12 May 2003; accepted 7 July 2003

Abstract

Three new cadmium(II) complexes: $[Cd(4\text{-}Clpy)_2(NCS)_2]_n$ (**1**), $[Cd(3\text{-}aldpy)(H_2O)(N_3)_2]_n$ (**2**) and $[Cd(3\text{-}CNpy)(N_3)_2]_n$ (**3**) (4-Clpy = 4-chloropyridine, 3-aldpy = 3-aldehyde-pyridine, and 3-CNpy = 3-cyanopyridine) have been synthesized and structurally characterized. The IR spectra of the complexes are measured and discussed. The single crystal X-ray diffraction revealed that the structure of **1** features μ-1,3-thiocyanate bridges and 1D chains. It consists of alternate octahedrally coordinated Cd atoms. Both Cd(1) and Cd(2) are surrounded by pairs of 4-Clpy, S atoms and N atoms of two di-μ-1,3 thiocyanato bridges in *trans* and *cis* arrangements, respectively. In complex **2** each octahedrally coordinated Cd binds two di-μ-1,1 azide bridges in a zigzag 1D chain and the other two positions are occupied by O and N atoms from aqua and 3-aldpy molecules, respectively. Hydrogen bonds of the types O–H···O and O–H···N are formed between aqua molecules and end nitrogen atoms of the μ-1,1 azide bridges generating 3D framework structure of **2**. The structure of **3** consists of $[Cd(N_3)_2]_n$ chains in which each octahedrally coordinated Cd atom is linked by two di-μ-1,1 azide bridges. These chains are cross-linked by μ-*N*,*N*′-3-CNpy bridges generating 2D systems for this complex.

Keywords: Cadmium(II) pseudohalides; Pyridine derivative complexes; Syntheses; Spectra; Crystal structures

1. Introduction

A wide variety of network topologies have been constructed through ligand design and the use of different transition metal geometries. This area of research has evolved rapidly in recent years as the coordination polymers may have interesting properties and applications, e.g., adsorption, ion exchange, non-linear optical and magnetic materials [1–4], and interesting topologies of one-, two-, or three-dimensional frameworks including helical [5,6], diamondoid and honeycomb [7], T-shaped [8], ladder [9–11] and of other frameworks have been established.

We have recently reported a number of cadmium(II) azido and thiocyanato coordination polymers with acetylpyridines, 4-bromopyridine [12,13], 3,5-lutidine [13], and 2-picoline-*N*-oxide [14]. Although cadmium(II) is octahedrally coordinated in all of these complexes, the bridging modes and topologies of the $[Cd(N_3)_2]_n$ or $[Cd(NCS)_2]_n$ chains are different. For example, $CdL_2(N_3)_2$ complexes adopt 2D honeycomb structure when L is 2-picoline-*N*-oxide but extended 2D framework for L = 2-methylpyrimidine [14]. Also $[Cd(4\text{-}Brpy)_2(NCS)_2]_n$ and $[Cd(3,5\text{-}lutidine)_2(N_3)_2]_n$ complexes have different topologies although both thiocyanate and azide ligands act in the μ-1,3 bridging fashion. We now extend our work to include the reaction of cadmium(II) thiocyanate and cadmium(II) azide with 4-chloropyridine (4-Clpy), 3-aldehydepyridine (3-aldpy) and

---

* Corresponding author. Tel.: +43-316-873-8234; fax: +2-03-3911794.
E-mail address: masidahmed@hotmail.com (M.A.S. Goher).

0277-5387/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00457-1

3-cyanopyridine (3-CNpy). This paper reports the synthesis and X-ray crystal structures of the title complexes for which 1D, 2D and 3D frameworks are established via covalent bonds and hydrogen bonds.

2. Experimental

2.1. Materials and instrumentation

Elemental analyses were carried out using a Perkin–Elmer analyzer [12]. Infrared spectra were recorded in a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets. 4-Chloropyridine hydrochloride, 3-aldehydepyridine and 3-cyanopyridine have been purchased from Aldrich and other chemicals were of analytical grade quality and used without further purification.

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

2.2. Synthesis

2.2.1. $[Cd(4\text{-}Clpy)_2(NCS)_2]_n$ (**1**)

This complex was prepared by mixing $3CdSO_4 \cdot 8H_2O$ (0.50 g, 1.95 mmol) in water (20 ml) with 4-chloropyridine (0.25 g, 3.33 mmol) in 5 ml methanol. An aqueous solution (5 ml) of KSCN (0.5 g, 8.626 mmol) was added dropwise with continuous stirring. The final mixture was filtered off and allowed to stand for several days in a refrigerator to deposit colorless crystals of the complex. Yield: 60%. Analyses: found %(Calc.): C, 31.6 (31.7); H, 2.0 (1.8); N, 12.4 (12.3); Cd, 24.2 (24.7). IR, KBr (cm^{-1}) (v, very; s, strong; m, medium; w, weak; br, broad): 2110vs, 2090vs 1610ms, 1585s, 1553ms, 1467vs, 1416vs, 1323s, 1194s, 1099vs, 1025vs, 797s, 690vs, 632s, 457ms, 402w.

2.2.2. $[Cd(3\text{-}aldpy)(H_2O)(N_3)_2]_n$ (**2**)

This complex was synthesized by mixing 3-aldehydepyridine (2 ml, 21.28 mmol) in 10 ml methanol with $3CdSO_4{\cdot}8H_2O$ (0.56 g, 2.18 mmol) in 30 ml H_2O followed by dropwise addition of aqueous solution (5 ml) of NaN_3(0.32 g, 5.0 mmol) with constant stirring. The final mixture was kept in a refrigerator for several weeks until good quality colorless crystals of the complex were obtained. Yield: 50%. Analyses: found %(Calc.): C, 22.1 (22.4); H, 2.3 (2.2); N, 29.8 (30.5); Cd, 35.2 (35.0). IR, KBr (cm^{-1}): 3250–3000 m,br, 2117vs, 2067vs, 1709vs, 1599vs, 1578s, 1431s, 1398s, 1339s, 1288ms, 1244ms, 1221vs, 1043ms, 839s, 797ms, 689s, 643ms, 593wm.

2.2.3. $[Cd(3\text{-}CNpy)(N_3)_2]_n$ (**3**)

Complex **3** was synthesized by adding 3-cyanopyridine (0.17 g, 16 mmol) to a solution of $3CdSO_4 \cdot 8H_2O$ (0.50 g, 1.95 mmol) in 30 ml H_2O followed by dropwise addition of aqueous solution (5 ml) of NaN_3 (0.32 g, 5.0 mmol) with constant stirring. The mixture was heated up to 85 °C to dissolve the ligand. After slow cooling to room temperature and filtration of first undefined precipitate colorless crystals of **3** were separated from mother liquor within a week. Yield: 50%. Analyses: found %(Calc.): C, 24.2 (24.0); H, 1.1 (1.3); N, 37.6 (37.3); Cd, 37.1 (37.4). IR KBr (cm^{-1}): 2239m, 2058vs, 2038vs, 1617m, 1592m, 1551w, 1466wm, 1417wm, 1329m, 1282m, 1191m, 873w, 818wm, 692m, 642m, 603wm, 515w, 426ms.

2.3. X-ray crystallography

Single crystal X-ray data were measured at 90(2) K on a modified STOE four circle diffractometer using graphite crystal-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The intensities were corrected for Lorentz-polarization effects and for absorption [range of normalized transmission factors: 1.000–0.489; 1.000–0.491 and 1.000–0.497, for **1**–**3**, respectively]. 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 program DIFABS [15] and SHELXTL/PC program package [16] were used for computations. Selected bond distances and bond angles are given in Tables 2–4, for complexes **1**–**3**, respectively.

3. Results and discussion

Three new complexes of Cd(II) thiocyanate or azide with 4-Clpy, 3-aldpy and 3-CNpy have been isolated. These complexes are insoluble in many polar solvents, e.g., water, MeOH, EtOH, acetone, etc., suggesting their polymeric nature. They are, however soluble in DMSO. As we found previously [13], the H NMR spectra of the DMSO solutions of these complexes indicate complete substitution of NCS$^-$ or N_3^- anion by DMSO solvent molecules.

3.1. Structures

The principle structural features of complex **1** are shown in Fig. 1, bond distances and bond angles are listed in Table 2. The structure consists of two crystallographically different Cd centers. The Cd(1) atom located at an inversion center is *trans*-coordinated by pairs

Table 1
Crystallographic data and processing parameters

Compound	1	2	3
Empirical formula	$C_{12}H_8CdCl_2N_4S_2$	$C_6H_7CdN_7O_2$	$C_6H_4CdN_8$
Formula mass	455.64	321.59	300.57
System	monoclinic	triclinic	monoclinic
Space group	*C2/c*	*P-1*	*P2₁/a*
a (Å)	20.979(9)	6.358(3)	6.529(3)
b (Å)	8.716(3)	8.207(4)	17.811(8)
c (Å)	19.239(9)	10.412(5)	8.195(4)
α (Å)	90	72.06(3)	90
β (°)	114.79(3)	80.80(3)	105.41(4)
γ (Å)	90	87.25(3)	90
V (Å^3)	3194(2)	510.2(4)	918.7(7)
Z	8	2	4
μ(Mo Kα) (mm^{-1})	1.959	2.138	2.355
$D_{\mathrm{Calc.}}$ (Mg/m^3)	1.895	2.093	2.173
Approximate crystal size (mm)	0.24 × 0.14 × 0.10	0.20 × 0.13 × 0.10	0.22 × 0.18 × 0.05
θ range (°)	3.00–25.00	2.80–25.00	2.82–24.99
Reflections collected	3492	2117	2056
Independent reflections/R_{int}	2809/0.0369	1795/0.0196	1593/0.0497
Parameters	192	156	136
Goodness-of-fit on F^2	1.068	1.117	1.202
$R1/wR2$	0.0431/0.1161	0.0247/0.0649	0.0687/0.2339
Largest peak/hole (e/Å^3)	0.941/−0.907	0.645/−1.028	1.164/−1.051

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

Cd(1)···Cd(2)	5.734(3)	Cd(1)–N(4)	2.284(4)
Cd(1)–N(1)	2.384(4)	Cd(1)–S(1)	2.705(2)
Cd(2)–N(3)	2.304(5)	Cd(2)–N(2)	2.381(5)
Cd(2)–S(2)	2.699(2)	S(1)–C(11)	1.652(6)
C(11)–N(3)	1.152(7)	S(2)–C(12)	1.643(6)
C(12)–N(4)	1.160(7)		
Cd(1)···Cd(2)···Cd(1B)	142.54(2)	N(4)–Cd(1)–N(1A)	90.7(2)
N(1)–Cd(1)–S(1A)	91.75(11)	N(4)–Cd(1)–S(1)	94.57(12)
N(3C)–Cd(2)–N(3)	173.8(3)	N(3)–Cd(2)–N(2C)	89.6(2)
N(3)–Cd(2)–N(2)	86.0(2)	N(2C)–Cd(2)–N(2)	88.2(2)
N(3C)–Cd(2)–S(2)	85.72(12)	N(3)–Cd(2)–S(2)	98.51(12)
N(2)–Cd(2)–S(2)	89.13(11)	N(3C)–Cd(2)–S(2C)	98.51(12)
N(2C)–Cd(2)–S(2C)	89.13(11)	N(2)–Cd(2)–S(2C)	171.29(11)
S(2)–Cd(2)–S(2C)	94.64(8)	C(11)–S(1)–Cd(1)	98.0(2)
N(3)–C(11)–S(1)	178.6(5)	C(11)–N(3)–Cd(2)	160.0(4)
C(12)–S(2)–Cd(2)	95.0(2)	N(4)–C(12)–S(2)	179.2(5)
C(12)–N(4)–Cd(1)	157.7(4)		

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

of S atoms [Cd(1)–S(1) = 2.705(2) Å], N atoms [Cd(1)–N(4) = 2.284(4) Å] from four NCS groups and N atoms [Cd(1)–N(1) = 2.384(4) Å] from two 4-Clpy ligands. Cd(2) center is on a diad and is *cis*-coordinated by similar pairs of S atoms [Cd(2)–S(2) = 2.699(2) Å], N atoms [Cd(2)–N(2) = 2.381(5) Å and Cd(2)–N(3) = 2.304(5) Å]. Thus, each of these two Cd centers is connected by two di-μ-1,3 thiocyanate bridges giving a zigzag 1D chain along [1 0 1] with successive *trans*, *cis*, *trans*, etc., arrangement and both have a CdN_4S_2 chromophore generating eight-membered $Cd_2(NCS)_2$ rings. This feature makes the structure unique. The acute angles between the planes of these rings and/or the pyridine rings are: ring [N(1)–Cl(1)] and ring [N(2)–Cl(2)] = 55.8(2)°, ring [N(2)–Cl(2)] and ring [N(2B)–Cl(2B)] = 89.51(16)°, ring [N(2B)–Cl(2B)] and [Cd(2)–N(3B)–S(2B)] = 80.68(12)°, chair conformation angles: [Cd(2)–N(3B)–S(2B)] and [S(2)–N(4)–S(1)–N(3)] = 13.54(20)°; [S(2)–N(4)–S(1)–N(3)] and [Cd(1)–S(1)–N(4)] = 17.71(18)°, and finally [Cd(2)–N(3B)–S(2B)] and [Cd(2)–N(3)–S(2)] = 85.61(5)°. The Cd···Cd distance of 5.734(3) Å closes well that reported for polymeric $[Cd(NCS)_2(4\text{-aba})_2]_n$ (4-aminobenzoic acid) (5.822(1) and 5.961(1) Å) containing also μ-1,3 thiocyanate bridges [17]. The structure of **1**, $[Cd(4\text{-Clpy})_2(NCS)_2]_n$, differs from that of the corresponding

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

Cd(1)···Cd(1A)	3.634(2)	Cd(1)···Cd(1B)	3.727(2)
Cd(1)–O(1)	2.293(3)	Cd(1)–N(11)	2.321(3)
Cd(1)–N(11A)	2.324(3)	Cd(1)–N(1)	2.363(3)
Cd(1)–N(21)	2.373(3)	Cd(1)–N(21B)	2.294(3)
N(11)–N(12)	1.204(4)	N(12)–N(13)	1.149(5)
N(21)–N(22)	1.209(4)	N(22)–N(23)	1.150(4)
O(1)···O(2C)	2.787(4)	O(1)···N(23D)	2.831(4)
Cd(1A)···Cd(1)···Cd(1B)	119.46(3)	O(1)–Cd(1)–N(21B)	96.17(11)
O(1)–Cd(1)–N(11)	90.08(11)	N(21B)–Cd(1)–N(11)	98.69(11)
O(1)–Cd(1)–N(11A)	99.98(11)	N(21B)–Cd(1)–N(11A)	163.26(12)
N(11)–Cd(1)–N(11A)	77.04(12)	O(1)–Cd(1)–N(1)	84.00(11)
N(21B)–Cd(1)–N(1)	99.93(11)	N(11)–Cd(1)–N(1)	160.95(10)
N(11A)–Cd(1)–N(1)	86.16(11)	O(1)–Cd(1)–N(21)	168.35(10)
N(21B)–Cd(1)–N(21)	73.99(12)	N(11)–Cd(1)–N(21)	97.47(12)
N(11A)–Cd(1)–N(21)	90.38(11)	N(1)–Cd(1)–N(21)	91.48(11)
N(12)–N(11)–Cd(1)	130.7(2)	N(12)–N(11)–Cd(1A)	121.5(2)
Cd(1)–N(11)–Cd(1A)	102.96(12)	N(13)–N(12)–N(11)	178.0(4)
N(22)–N(21)–Cd(1B)	132.1(2)	N(22)–N(21)–Cd(1)	121.7(2)
Cd(1B)–N(21)–Cd(1)	106.01(12)	N(23)–N(22)–N(21)	178.8(4)
O(2C)···O(1)···N(23D)	125.34(13)		

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

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

Cd(1)···Cd(1A)	3.560(2)	Cd(1)–N(11A)	2.257(7)
Cd(1)–N(21)	2.287(8)	Cd(1)–N(21A)	2.313(7)
Cd(1)–N(1)	2.316(8)	Cd(1)–N(11)	2.351(6)
Cd(1)–N(2)	2.479(9)	N(11)–N(12)	1.211(7)
N(11)–Cd(1B)	2.257(7)	N(12)–N(13)	1.152(8)
N(21)–N(22)	1.225(7)	N(21)–Cd(1B)	2.313(7)
N(22)–N(23)	1.145(8)		
N(11A)–Cd(1)–N(21)	96.8(3)	N(11A)–Cd(1)–N(21A)	79.3(2)
N(21)–Cd(1)–N(21A)	103.0(2)	N(11A)–Cd(1)–N(1)	92.3(3)
N(21)–Cd(1)–N(1)	161.5(3)	N(21A)–Cd(1)–N(1)	94.5(3)
N(11A)–Cd(1)–N(11)	105.5(2)	N(21)–Cd(1)–N(11)	78.0(2)
N(21A)–Cd(1)–N(11)	175.0(3)	N(1)–Cd(1)–N(11)	84.2(2)
N(11A)–Cd(1)–N(2)	160.9(2)	N(21)–Cd(1)–N(2)	84.5(3)
N(21A)–Cd(1)–N(2)	81.8(3)	N(1)–Cd(1)–N(2)	92.2(3)
N(11)–Cd(1)–N(2)	93.4(2)	N(12)–N(11)–Cd(1B)	128.4(6)
N(12)–N(11)–Cd(1)	115.0(5)	Cd(1B)–N(11)–Cd(1)	101.1(2)
N(13)–N(12)–N(11)	177.5(8)	N(22)–N(21)–Cd(1)	122.8(6)
N(22)–N(21)–Cd(1B)	126.7(6)	Cd(1)–N(21)–Cd(1B)	101.4(3)
N(23)–N(22)–N(21)	176.5(11)		

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

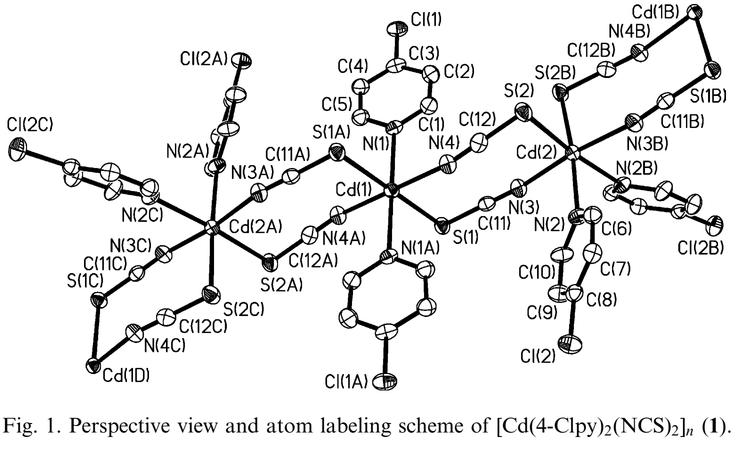

Fig. 1. Perspective view and atom labeling scheme of [Cd(4-Clpy)$_2$(NCS)$_2$]$_n$ (**1**).

$[Cd(4\text{-}Brpy)_2(N_3)_2]_n$ (**4**) [13]. In complex **4** each octahedrally coordinated Cd atom binds two *trans* pyridine ligands and two *trans* nitrogen or sulfur atoms from four μ(N,S) bridging NCS^- groups. The other end atoms of these thiocyanato ligands link four different Cd atoms forming a 2D layer structure.

The atom labeling scheme for complex **2** is shown in Fig. 2; selected bond lengths and bond angles are given in Table 3. The structure features six coordinate Cd(II) centers. Each Cd is linked by four nitrogen atoms N(11), N(11A), N(21), N(21B) from double di-μ-1,1 azide bridges [Cd–N from 2.294(3) to 2.373(3) Å] forming cyclic four-membered Cd_2N_2 rings. The other coordination sites are occupied by a nitrogen atom N(1) from 3-aldpy [Cd–N 2.363(3) Å] and oxygen atom O(1) from aqua molecule [Cd–O 2.293(3) Å] both are in *cis* arrangement to each other. The resulting 1D system is running along the *b*-axis of the unit cell. The Cd···Cd distances of 3.634(2) and 3.727(2) Å within the four-membered Cd_2N_2 rings are very close to those reported in the structure of $[Cd(2\text{-}Acpy)(N_3)_2]_n$ (2-Acpy = 2-acetylpyridine) 3.561(1) Å [12] and in $[Cd(N_3)_2(2\text{-}picNO)_2]_n$ (2-PicNO = 2-picoline-*N*-oxide) 3.652(2) Å [14]. The Cd–N(N_3) bond length and Cd–O(H_2O) (Table 3) are within the range of 2.27–2.34 Å reported for other cadmium(II) azide complexes containing di-μ-1,1 azide bridges [12–14]. Although 3-aldpy is potentially a bidentate ligand, it acts as a monodentate one, and thus complex **2** crystallizes with an aqua ligand to complete the coordination number of Cd centers to be six. Hydrogen bonds of the type O–H···O between O(1) of aqua molecule and O(2) of two aldehyde groups [O(1)···O(2C) = 2.787(4) Å] and of the type O–H···N between oxygen atom of aqua molecules and the end nitrogen N(23) of μ-1,1 azide bridges [O(1)···N(23D) = 2.831(4) Å]. These hydrogen bonds connect the different 1D $Cd(N_3)_2$ chains generating a 3D network structure for **2** (Fig. 3).

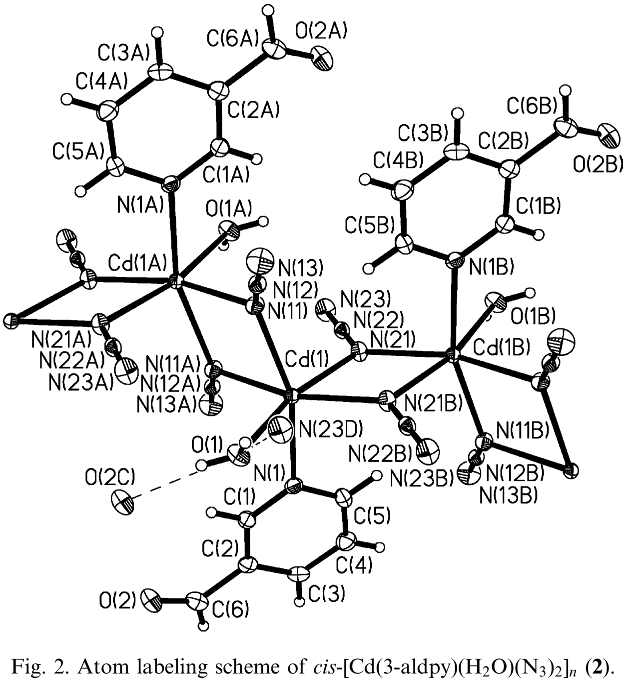

Fig. 2. Atom labeling scheme of *cis*-$[Cd(3\text{-}aldpy)(H_2O)(N_3)_2]_n$ (**2**).

Fig. 4 illustrates the principle structural feature of complex **3**, bond distances and bond angles are collected in Table 4. The structure of **3** features 1D $[Cd(N_3)_2]_n$ chains running along *a*-axis, μ-1,1 azide bridges and six-coordinated Cd(II) atoms. In the chain each Cd center is coordinated by four nitrogen atoms from two pairs of N_3-groups [Cd–N from 2.257(7) Å to 2.351(5) Å]. Each pair of adjacent metal atoms bridged by a pair of μ-1,1 N_3-groups forms four-membered Cd_2N_2 rings with intra Cd···Cd distance of 3.560(2) Å. The chains are further connected by *N*,*N*′-bridging 3-CNpy ligands generating 2D systems parallel *a*/*c* planes (Fig. 4). Thus, each Cd center is connected by a pyridine N atom [Cd–N = 2.316(8) Å] from a 3-CNpy and by a cyano N atom [Cd–N = 2.479(9) Å] from the other side of the $[Cd_2(N_3)_2]_n$ chain. The intra-layer Cd···Cd distance via the 3-CNpy ligands is 8.196(4) Å and the interlayer Cd···Cd distance along *b*-axis is 6.529(3) Å. The present structure differs from those of $[CdLN_3)_2]_n$ complexes for L = 2-picoline-*N*-oxide and 4-methylpyrimidine, although both contain distorted octahedral Cd centers and bridging organic ligands [14]. In these later structures the metal atoms are linked by alternate di-μ-1,1 and di-μ-1,3 azide bridges in *cis* arrangements and these chains are connected by 2-picoline-*N*-oxide giving honeycomb 2D framework or by 4-methylpyrimidine forming extended 2D network [14].

3.2. IR spectra

The IR spectrum of **1** exhibits two very strong bands at 2110 and 2090 cm^{-1} due to ν(CN) mode in addition to medium to strong bands at 797 and 690 cm^{-1} related to ν(CS) mode. These features are consistent with the results of the structure analysis given above as the 1,3-N,S-bridging thiocyanate is expected to show two ν(CN) bands above and below 2000 cm^{-1} as well as two ν(CS) bands [18–22]. This is confirmed by the appearance of two δ(NCS) bands at 457 and 402 cm^{-1}. The appearance of the ν(C = O) band at 1709 cm^{-1} in the IR spectra of both complex **2** and free 3-aldpy, in addition to the normal shifts of other pyridine vibrations, suggests that 3-aldpy behaves as a monodentate ligand coordinating via the hetero nitrogen atom only. The spectrum of **2** also shows two very strong bands at 2117 and 2067 cm^{-1}. The positions of these bands suggest μ-1,1 bridging azido groups [23], although it is higher than expected for Δd (difference between N_α–N_β and N_β–N_γ) of about 0.06 Å found for both azide groups (see Table 3) on the basis of Δd $\nu_{as}N_3$ relationship mentioned earlier [24]. The asymmetric nature of the azide is

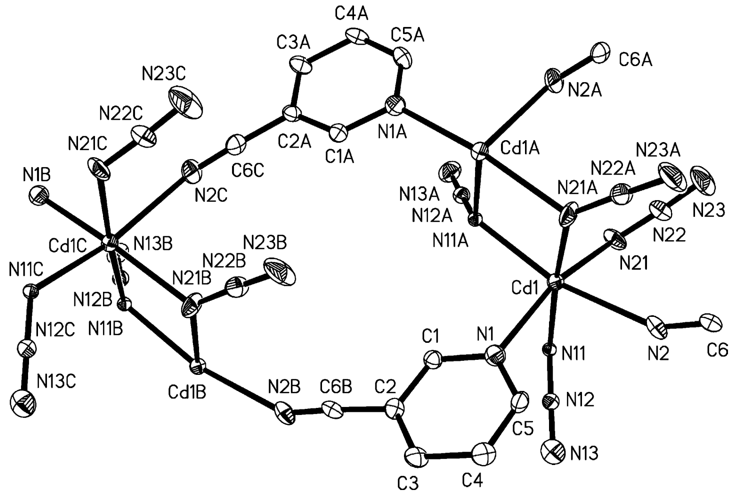

Fig. 3. Perspective view of $[Cd(3\text{-}CNpy)(N_3)_2]_n$ (**3**) with atom labeling scheme.

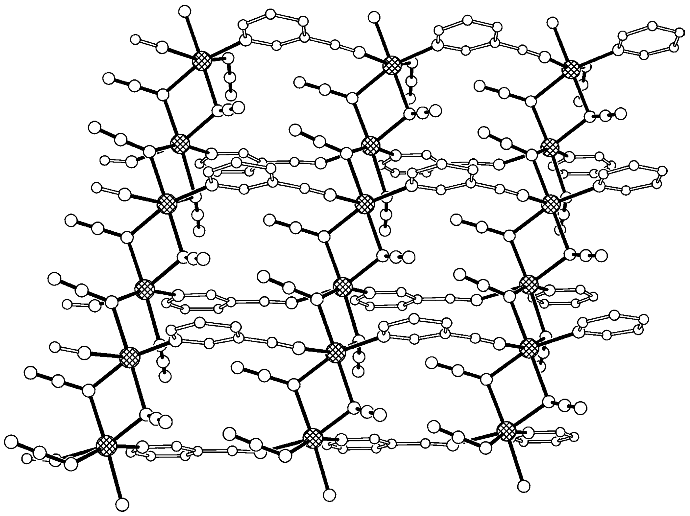

Fig. 4. View onto a layer of $[Cd(3\text{-}CNpy)(N_3)_2]_n$ (**3**).

confirmed by the appearance of a medium to strong band at 1288 cm^{-1}, due to ν_sN_3 mode. The hydrogen bonded aqua molecule is indicated by the broad medium to strong band 3550–3000 cm^{-1}. The IR spectrum of **3** shows a weak band at 2239 cm^{-1} (νCN of 3-CNpy) and two very strong bands at 2058 and 2038 cm^{-1}, due to $\nu_{as}N_3$. The positions of the last two bands, particularly the lower frequency band, are not consistent with μ-1,1 azide bridge of $\Delta d = 0.08$ and 0.059 Å. The appearance of such a lower frequency band (2038) may be due to coupling between the vibrations of the two azide groups.

4. Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition numbers: CCDC-210171–CCDC-210173 for **1**–**3**, respectively.

Acknowledgements

F.A.M. thanks Prof. Kratky and Prof. Belaj (Univ. Graz) for the use of the STOE 4-circle diffractometer.

References

[1] B.F. Hoskins, R. Robson, J. Chem. Soc. 112 (1990) 1564.
[2] M. Fujita, Y.J. Kwan, S. Washizu, K. Ogurs, J. Am. Chem. Soc. 116 (1994) 1151.
[3] O.M. Yaghi, J. Li, J. Am. Chem. Soc. 117 (1995) 10401.
[4] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem., Int. Ed. Engl. 38 (1999) 2638.
[5] M.A. Withersby, A.J. Blake, N.R. Champness, P. Hubberstey, W.-S. Li, M. Schroder, Angew. Chem., Int. Ed. Engl. 36 (1997) 2327.
[6] L. Carlucci, G. Ciani, D.M.V. Gudenberg, D.M. Proserpio, A. Sironi, Inorg. Chem. 36 (1997) 3812.
[7] M.-L. Tong, X.-L. Yu, X.-M. Chen, J. Chem. Soc., Dalton Trans. (1995) 5.

[8] M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen, Inorg. Chem. 37 (1998) 2645.
[9] L.R. Mc Gillavry, S. Subramamian, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1994) 1325.
[10] M. Fujita, Y.J. Kwan, O. Sataki, K. Yamaguchi, K. Ogura, J. Am. Chem. Soc. 117 (1995) 7287.
[11] A.J. Blake, N.R. Champness, A. Khlobystov, D.A. Lemenovskii, W.-S. Li, M. Schroder, Chem. Commun. (1997) 2027.
[12] M.A.S. Goher, F.A. Mautner, M.A.M. Abu-Youssef, A.K. Hafez, A.M.A. Badr, J. Chem. Soc., Dalton Trans. (2002) 3309.
[13] M.A.S. Goher, F.A. Mautner, A.K. Hafez, M.A.M. Abu-Youssef, C. Gspan, A.M.A. Badr, Polyhedron 22 (2003) 975.
[14] F.A. Mautner, C. Gspan, A.K. Hafez, M.A.S. Goher, Inorg. Chim. Acta, submitted.
[15] H. Walker, D. Stuart, Acta Crystallogr. A 39 (1983) 158.
[16] SHELXTL/PC 5.03, Siemens Analytical Automation Inc., Madison, WI, 1995.
[17] H.-J. Chen, X.-M. Chen, Inorg. Chim. Acta 329 (2002) 13.
[18] (a) P.C.H. Mitchell, R.J.P. Williams, J. Chem. Soc. (1960) 1912;
(b) A. Tramer, J. Chem. Phys. 59 (1962) 232.
[19] J. Lewin, R.S. Nyholm, P.N. Smith, J. Chem. Soc. (1961) 4590.
[20] A. Subatini, I. Bertini, Inorg. Chem. 4 (1965) 959.
[21] (a) R.J.H. Clerk, C.S. Williams, Spectrochim. Acta 22 (1966) 1081;
(b) M. Aslam, W.H.S. Assai, Inorg. Nucl. Chem. Lett. 7 (1971) 96.
[22] M.A.S. Goher, Coll. Czech. Chem. Commun. 42 (1977) 1478.
[23] (a) J.L. Manson, A.M. Arif, J.S. Miller, Chem. Commun. (1999) 1479;
(b) J. Ribas, M. Monfort, B.K. Ghosh, X. Solans, Angew. Chem., Int. Ed. Engl. (1994) 2087;
(c) X. Hao, Y. Wei, S.-W. Zhang, Chem. Commun. (2000) 2271.
[24] (a) I. Agrell, Acta Chem. Scand. 25 (1971) 2965;
(b) M.A.S. Goher, Acta Chim. Hung. 127 (1990) 213.