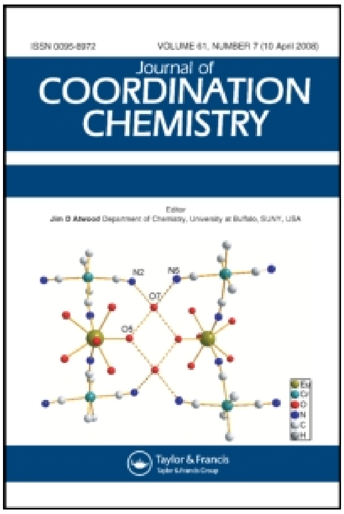

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Synthesis and crystal structure of a new one-dimensional cadmium(II)-azide system with phenyl-2-pyridyl ketone

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Synthesis and crystal structure of a new one-dimensional cadmium(II)–azide system with phenyl-2-pyridyl ketone

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A new one-dimensional (1-D) cadmium(II) complex $[Cd(ppk)(N_3)_2]_n$ (**1**) has been synthesized and characterized. X-ray crystal structure study reveals that **1** is composed of a 1-D cadmium(II) chain with double $\mu_{1,1}$ azido bridges. Three different cadmiums, Cd(1), Cd(2), and Cd(3), may be found along the chain.

Keywords: Crystal structure; Cadmium(II) complex; Phenyl-2-pyridyl ketone; Azido bridges; Coordination polymer

1. Introduction

Metal-azido-bridged systems with organic ligands show a variety of new materials with interesting structures and properties, including magnetic features. As a versatile bridging ligand, azide links two or more metal ions in various modes, μ-1,1 (end-on, EO), μ-1,3 (end-to-end, EE), μ-1,1,1, μ-1,1,3, and so on, giving rise to a variety of 0-, 1-, 2-, and 3-D polynuclear complexes [1–20].

There are numerous investigations on manganese(II) [21–24] and copper(II) [25–27] azido complexes with pyridine derivatives and other ligands, but only a few examples of corresponding cadmium(II) complexes [28, 29]. These cadmium complexes contain either μ-1,1 (end-on), μ-1,3 (end-to-end) or μ-1,1,1, and μ-1,1,3 bridging azides.

Following our research on coordination compounds with 2-pyridyl ketones [30–34], we report here the synthesis, spectral, and structural studies of a new 1-D cadmium(II)–azide system with phenyl-2-pyridyl ketone (ppk) of formula $[Cd(ppk)(N_3)_2]_n$ (**1**).

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2. Experimental

2.1. *Materials and apparatus*

All the starting chemicals were of analytical reagent (AR) grade and used as received.

Caution: Azido compounds of metal ions are potentially explosive. Only a small amount of the materials should be prepared and handled with care.

Elemental analyses (C, H, and N) were performed on a Costech ECS 4010 elemental analyzer. Infrared (IR) spectra were recorded as KBr pellets with a Bio-Rad FTS 135 spectrometer from 4000–400 cm^{-1}. Single-crystal X-ray diffraction measurements for **1** were performed on a Stoe Imaging Plate Diffraction System (STOE IPDS II) using graphite-monochromated Mo-Kα radiation.

2.2. *Synthesis*

The synthesis of the cadmium(II) compound was carried out by slow diffusion reaction. An aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (1 mmol, 0.308 g, 5 mL water) was layered carefully by 3 mL tetrahydrofuran (THF), and then a methanol solution of ppk (1 mmol, 0.183 g, 5 mL methanol) and an aqueous solution of NaN_3 (2 mmol, 0.13 g, 1 mL water). The tube was sealed and then left undisturbed at room temperature. Three days later, colorless needles appeared, suitable for X-ray determination.

$[Cd(ppk)(N_3)_2]_n$ (**1**): Colorless needles. Yield 48%. Anal. Calcd for $C_{12}H_9CdN_7O$ (%): C, 37.99; H, 2.37; and N, 25.86. Found: C, 37.39; H, 2.83; and N, 25.29. IR (cm^{-1}, KBr): 2934 (w), 2852 (w), 2038 (vs), 1644 (s), 1588 (m), 1321(s), 1178 (m), 953 (m), and 697 (s).

2.3. *Single-crystal X-ray diffraction*

Single-crystal X-ray diffraction was used for crystal structure determination of the cadmium(II) compound. XRD data were collected on a STOE IPDS II image plate detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Data collections: Stoe X-AREA [35]. Cell refinement: Stoe X-AREA [35]. The structures were solved by direct methods and refined with anisotropic displacement parameters based on F^2 using SHELXS 97 [36] and SHELXL 97 [37] programs. Significant bond parameters for **1** are given in table 1.

3. Results and discussion

3.1. *Synthesis and IR spectrum*

$[Cd(ppk)(N_3)_2]_n$ (**1**) was obtained by slow diffusion of $Cd(NO_3)_2$, ppk and NaN_3 in 1 : 1 : 2 molar ratio. Diffusion between the aqueous solution of Cd(II) and methanol solution of ppk and little aqueous NaN_3 led to large needles of coordination polymer **1**.

The IR spectrum provides evidence of ligand coordination through pyridine nitrogen and oxygen of the carbonyl. The strong peak at 1644 cm^{-1} is in agreement with the

Table 1. Crystallographic data, details of data collection, and structure refinement parameters for **1**.

Compound	$[Cd(ppk)(N_3)_2]_n$
Empirical formula	$C_{36}H_{27}Cd_3N_{21}O_3$
M ($g\,mol^{-1}$)	1138.99
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions (Å, °)	
a	13.6132(6)
b	16.6458(5)
c	19.4962(7)
α	90.00
β	97.980(3)
γ	90.00
V (Å^3), Z	4375.1(3), 4
Calculated density ($g\,cm^{-3}$)	1.729
Absorption coefficient (mm^{-1})	1.507
$F(000)$	2232
Goodness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0463$, $wR_2 = 0.0919$
R indices (all data)	$R_1 = 0.0733$, $wR_2 = 0.1026$
Largest difference peak and hole (e Å^{-3})	1.047 and −0.762

stretching vibration of C=O, while the medium absorption which is observed at 1588 cm^{-1} is assigned to vibration of the C=N group [38].

Moreover, the infrared spectrum of $[Cd(ppk)(N_3)_2]_n$ displays characteristic bands of the azide bridges. In the region expected for ν_{as} (N_3), the complex exhibits only one very strong band at 2038 cm^{-1}. This band is accompanied by a strong band at 1321 cm^{-1}, assigned to the symmetric stretching vibration of azide group, suggesting the presence of μ-1,1 (end-on, EO) bridging mode of azide [39].

3.2. *Description of crystal structure*

Crystallographic data for **1** are given in table 1. Selected bond lengths and angles are given in table 2.

A view of the basic unit of $[Cd(ppk)(N_3)_2]_n$ is shown in figure 1. The structure consists of neutral chains of cadmiums linked by μ-1,1-azido bridges. The cadmiums are pseudooctahedral similar to cadmium(II) found in analogous complexes with methyl-2-pyridyl ketone [28, 29] coordinated by a chelating N, O 2-benzoylpyridine, and four azido ligands which act as *end-on* double bridges with the two neighboring cadmium ions. The azido ligands are linear and show asymmetric N–N distances, close to 1.19/1.13 Å.

Three crystallographically different cadmium ions, Cd(1), Cd(2), and Cd(3), form a Cd_3 subunit in the asymmetric unit (figure 1) in the same way as it occurs in the $[Cd_3(L^1)_2(N_3)_6(H_2O)(CH_3OH)_{0.5}]_n$, L^1 = 2-acetylpyridine [29]. Two equivalent trinuclear subunits related by an inversion center placed between Cd(3) and Cd(3′) are interlinked by two μ-1,1-azido bridges to form a hexanuclear unit (figure 1). The types

Table 2. Selected bond distances and angles for **1**.

N1–Cd1	2.299(3)	N1–Cd1–N4	96.94(10)	N4–Cd2–N20	153.82(10)
N1–Cd1	2.323(2)	N1–Cd1–N7	113.95(10)	N13–Cd2–N20	85.51(9)
N4–Cd1	2.308(2)	N1–Cd1–N19	78.27(9)	N7–Cd2–O3	87.85(10)
N7–Cd1	2.312(3)	N4–Cd1–N7	93.91(10)	N10–Cd2–O3	160.43(9)
N19–Cd1	2.317(3)	N4–Cd1–N19	100.11(9)	N4–Cd2–O3	86.10(10)
O1–Cd1	2.442(2)	N7–Cd1–N19	152.13(10)	N13–Cd2–O3	93.30(9)
N4–Cd2	2.299(3)	N1–Cd–N1	78.65(10)	N20–Cd2–O3	68.29(9)
N7–Cd2	2.281(2)	N4–Cd1–N1	167.39(10)	N13–Cd3–N16	114.05(10)
N10–Cd2	2.298(3)	N7–Cd1–N1	92.63(10)	N13–Cd3–N16	98.17(10)
N13–Cd2	2.352(2)	N19–Cd1–N1	92.02(10)	N16–Cd3–N16	78.29(11)
N20–Cd2	2.368(3)	N1–Cd1–O1	161.69(9)	N13–Cd3–N21	92.53(10)
O3–Cd2	2.436(2)	N4–Cd1–O1	90.48(11)	N16–Cd3–N21	153.41(10)
N10–Cd3	2.372(2)	N7–Cd1–O1	83.91(9)	N16–Cd3–N21	99.66(10)
N13–Cd3	2.293(3)	N19–Cd1–O1	68.24(9)	N13–Cd3–N10	79.84(9)
N16–Cd3	2.294(3)	N1–Cd1–O1	97.28(10)	N16–Cd3–N10	94.95(9)
N16–Cd3	2.298(3)	N7–Cd2–N10	101.86(9)	N16–Cd3–N10	171.55(9)
N21–Cd3	2.348(3)	N7–Cd2–N4	79.08(9)	N21–Cd3–N10	88.65(9)
O2–Cd3	2.405(2)	N10–Cd2–N4	112.25(10)	N13–Cd3–O2	159.35(9)
Cd1···Cd2	3.556	N7–Cd2–13	169.75(10)	N16–Cd3–O2	85.44(10)
Cd2···Cd3	3.568	N10–Cd2–N13	80.17(9)	N16–Cd3–O2	92.28(10)
Cd3···Cd3′	3.561	N4–Cd2–N13	90.83(9)	N21–Cd3–O2	68.08(9)
		N7–Cd2–N20	104.33(10)	N10–Cd3–O2	92.22(9)
		N10–Cd2–N20	92.69(9)	Cd1···Cd2···Cd3	133.73
				Cd2···Cd3···Cd3′	133.30

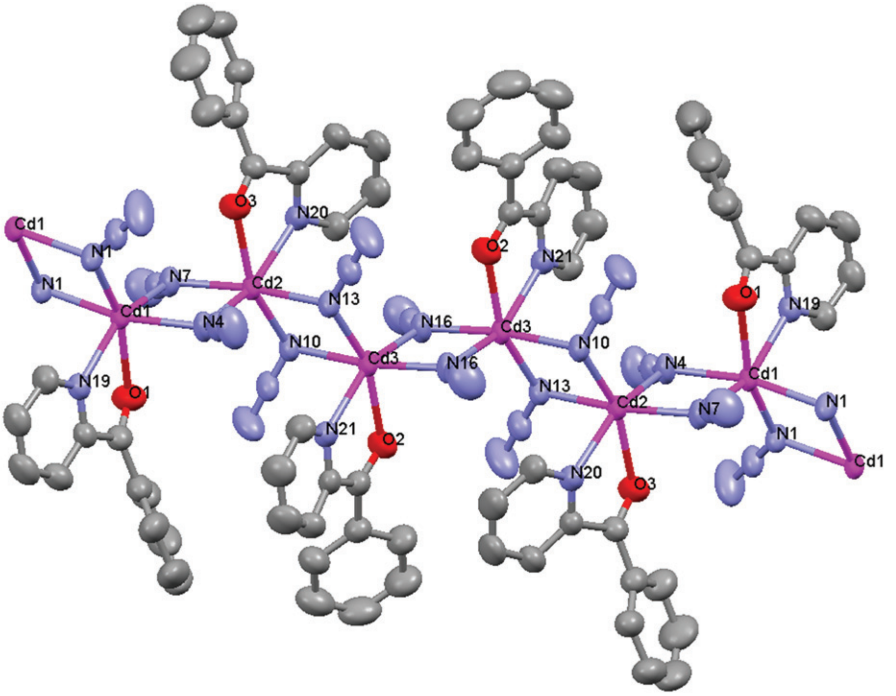

Figure 1. Perspective view with atom labeling scheme of **1** (ellipsoids at the 50% probability level).

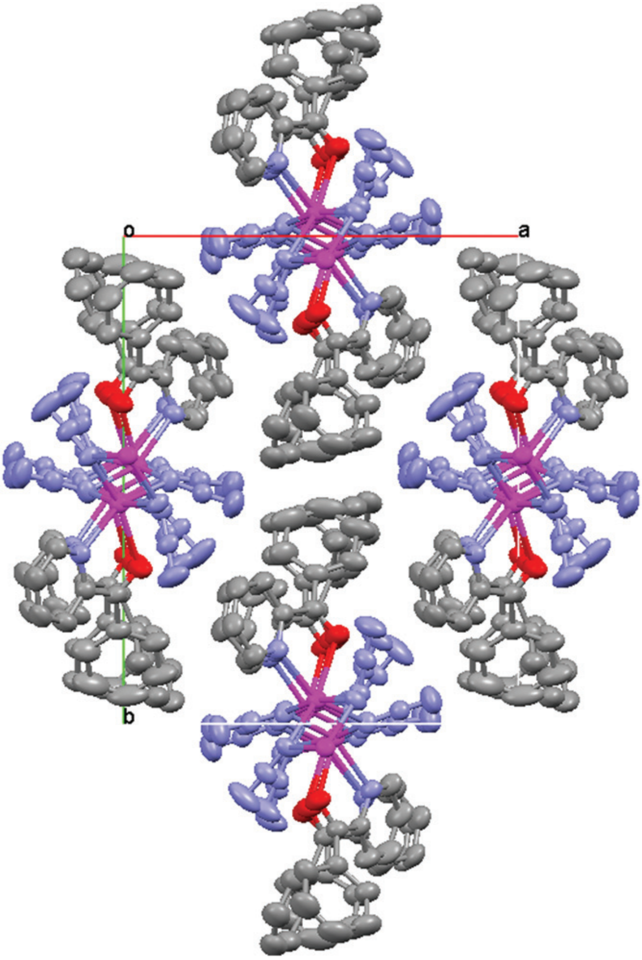

Figure 2. Packing diagram for **1** along the *c*-axis.

of bridges in the $[Cd_3(L^1)_2(N_3)_6(H_2O)(CH_3OH)_{0.5}]_n$ [29] are μ-1,1,1 and four central Cd(II) ions from the hexanuclear unit exhibit a dicubane-like structure with two missing vertices [29]. In our compound, neighboring hexanuclear units in the *b*-direction are further interlinked by two *end-on* azido bridges generating a 1-D chain extending along the *b*-direction. In another cadmium(II) complex [29], the 1-D chain extends along the *a*-direction, while in $[Cd(2\text{-Acpy})(N_3)_2]_n$ (2-Acpy = 2-acetylpyridine) [28], each unit is linked to another four units by four μ-1,3 azido ligands giving 2-D polymeric chains.

Bond angles in the two centrosymmetric four-member rings Cd(1)–N(1)–Cd(1) and Cd(3)–N(16)–Cd(3′) are 101.3(4)° and 101.7(3)°, respectively, whereas the bond angles for the remaining noncentrosymmetric rings are Cd(1)–N(7)–Cd(2) and Cd(1)–N(4)–Cd(2) 101.4(8)° and 101.0(3)°, and Cd(2)–N(13)–Cd(3) and Cd(2)–N(10)–Cd(3), 100.3(5) and 99.6(0)°. The four different Cd $\cdots$ Cd distances range between 3.556 and 3.575 Å. Because of the bulk 2-benzoylpyridine ligand, the chains are well isolated, the minimum Cd $\cdots$ Cd interchain distance being 10.200 Å (figure 2).

4. Conclusions

We have synthesized and structurally characterized a new 1-D Cd(II)–azide coordination polymer built from Cd_6 units, in which three crystallographically different cadmium ions, Cd(1), Cd(2), and Cd(3), form two Cd_3 subunits separated by an inversion center. Hexanuclear units are interlinked by two *end-on* azido bridges generating a 1-D chain extending along the *b*-direction.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC number: 780611. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/deposit (or from the Cambridge Crystallographic Data Centre, 12 Union Road, CAMBRIDGE, CB2 1EZ, UK; Tel: (44) 01223 762910; Fax: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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The diffraction data for the title compound were collected on a STOE IPDS II at the Laboratory of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, Romania. The authors thank Mr Marius Andruh and Mr Augustin Madalan for their useful discussions and for their help they provided in writing this article.

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