

STRUCTURE OF ORGANIC
COMPOUNDS

Synthesis and Crystal Structure of a 3D Cd(II)
Coordination Polymer Assembled with Itaconate
and 1,2-Bis(4-pyridyl)ethane

C. García-Hernández^a, A. Téllez-López^{a,b}, D. Martínez-Otero^b,
and V. Sánchez-Mendieta^{b,*}

^a Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón y Paseo Tollocan,
Toluca, Estado de México, 50120 México

^b Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Ixtlahuaca Km. 14.5,
San Cayetano, Toluca, Estado de México, 50200 México

* e-mail: vsanchezm@uaemex.mx

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Abstract—The three-dimensional cadmium coordination polymer $\{[\text{Cd}_4(\text{H}_2\text{O})_2(\text{ita})_4(\text{bpe})_6] \cdot (\text{H}_2\text{O})_{26}\}_n$ (**1**) (ita = itaconate; bpe = 1,2-bis(4-pyridyl)ethane) was obtained by self-assembly solution reaction under ambient conditions and characterized by elemental analysis, IR spectroscopy, and X-ray single crystal diffraction. Compound **1** crystallizes in the orthorhombic system with space group $P2_12_12_1$. Cd centers exhibit distorted octahedral and distorted pentagonal bipyramidal coordination geometries. Polymer **1** demonstrates a new 3D topology.

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INTRODUCTION

Over the past three decades, studies of the structure and physicochemical properties of coordination polymers have expanded considerably. This tendency has been mainly promoted by an interesting relationship between the hybrid organic-inorganic nature of coordination polymers and their unique properties, which leads to different potential applications in areas such as catalysis, chemosensing, magnetism, gas storage, filtration, etc. [1–6]. Particularly, cadmium coordination polymers are mainly used due to their inherent photophysical properties [7, 8], which can transform them into functional hybrid materials useful as sensor photoluminescent probes for a variety of analytes, from solvents and metal ions to other analytes [9–11]. To date, there are few reports about Cd(II)-coordination polymers developed using itaconate as a bridging ligand (seven entries in the CSD) [12–17]. As a matter of fact, compared to other dicarboxylic acids, itaconic acid has only been used to obtain a still relatively small number of crystalline coordination polymers [18–21]. Therefore, the use of itaconate in combination with an N-bridging ligand such as 4,4'-bipyridine or their derivatives can be a feasible strategy to assemble 3D transition metal coordination polymers.

Here, the synthesis under ambient conditions and the crystal molecular structure of a novel 3D Cd(II) coordination polymer (**1**) containing itaconate (ita) and 1,2-bis(4-pyridyl)ethane (bpe) as bridging ligands are analyzed.

EXPERIMENTAL

Materials and Measurements

All chemicals were of analytical grade, purchased commercially (Sigma-Aldrich) and used without further purification. The synthesis was carried out under aerobic and ambient conditions. Elemental analyses for C, H, N were performed by standard methods using a Vario Micro-Cube analyzer. The IR spectrum of the complex was determined using a Bruker Tensor 27 spectrophotometer, with Platinum ATR, in the range 4000–400 cm^{-1} .

Synthesis

A solution of itaconic acid (0.0130 g, 0.1 mmol) in methanol (5 mL) was added with stirring to an aqueous solution (5 mL) of sodium hydroxide (0.0078 g, 0.2 mmol). Then an aqueous solution (5 mL) of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.0308 g, 0.1 mmol) was added to

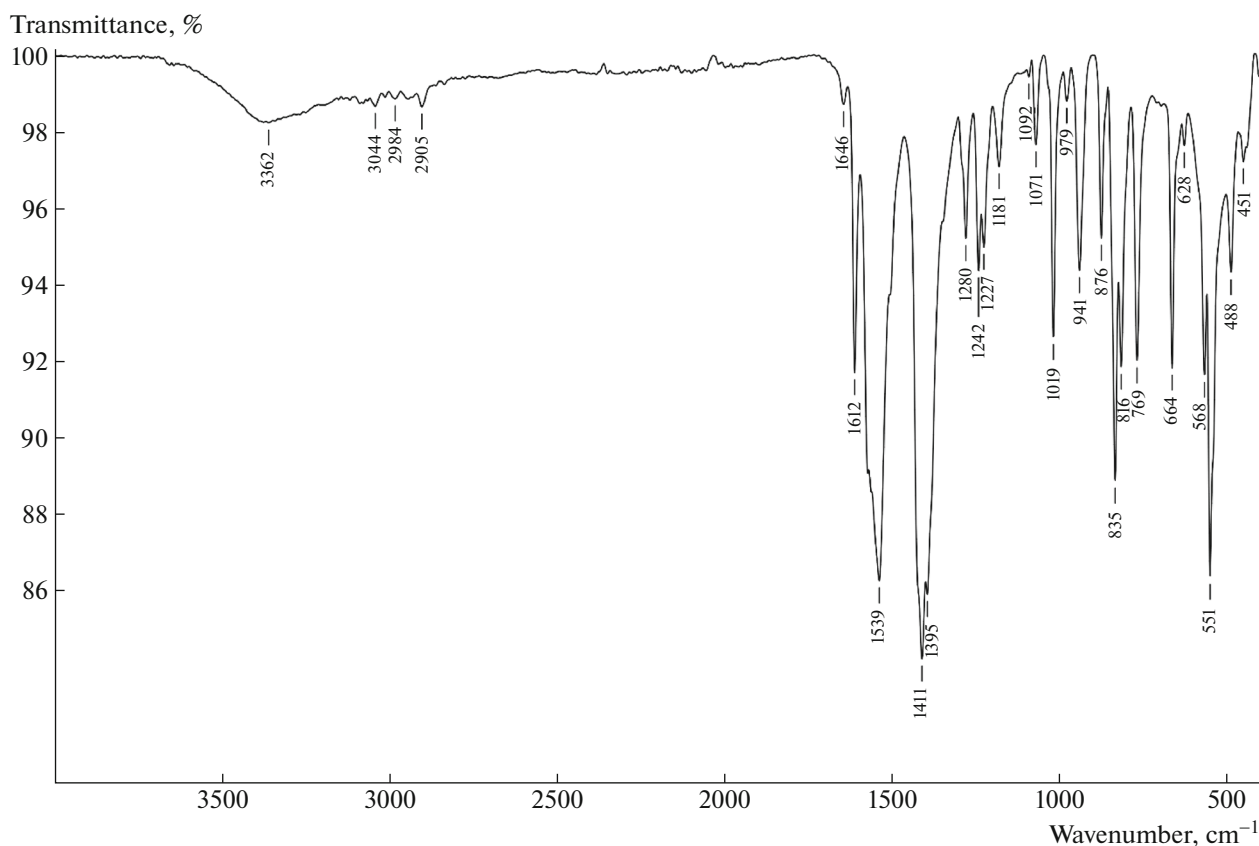


Fig. 1. IR spectrum of compound 1.

a solution of 1,2-bis(4-pyridyl)ethane (0.0184 g, 0.1 mmol) in methanol (5 mL). Finally, both solutions were combined, and a transparent solution was obtained. Three days later, translucent white crystals were obtained, then filtered and washed with 50 : 50 deionized water-methanol solution and air dried. Elemental analysis: calculated for $C_{92}H_{144}Cd_4N_{12}O_{44}$: C 42.84, H 5.63, N 6.52 wt %. Found: C 42.55, H 5.74, N 6.48 wt %. IR: 3362 (w, br) O–H stretching; 2905 (w) C–H stretching; 1612 (m) COO stretching unsymmetrical; 1539 (s) COO stretching unsymmetrical; 1411 (s) COO stretching symmetrical; 1395 (s) COO stretching symmetrical; 1242 (m) C–O stretching; 1019 (m) C–O stretching; 835 (s), 769 (m), 664 (m) and 551 (s) aromatic sp^2 CH bending (1,2-bis(4-pyridyl)ethane ligand), cm^{-1} . IR spectrum of compound 1 is shown in Fig. 1.

Structure Studies

X-ray diffraction data were collected on a Bruker SMART APEX DUO CCD diffractometer (MoK_{α} , $\lambda = 0.71073 \text{ \AA}$) at 100(2) K. The crystal was coated with hydrocarbon oil, picked up with a nylon loop,

and immediately placed in a cold nitrogen stream ($-173^{\circ}C$) on the diffractometer. Frames were collected during omega-scanning, integrated using the SAINT program and semiempirical absorption correction (SADABS) [22]. The structure was solved by direct methods (SHELXT) [23] and refined by full-matrix least-squares on F^2 using the SHELXL-97 [24] and the SHELXLE graphical user interface [25]. The weighted R factor and the goodness-of-fit indicator were based on F^2 . All atoms, except for hydrogen, were refined in the anisotropic approximation of their displacement parameters. The hydrogen atoms from C–H bonds were placed in idealized geometric positions and refined with the U_{iso} parameter of the parent atom using the riding model. The hydrogen atoms of water molecules were localized from the residual electron density map and fixed at standard distances (0.84 \AA) using DFIX instructions. The disordered ligand moiety in the compound was refined using geometry (SADI, DFIX, SAME, FLAT) and U_{ij} restraints (SIMU, RIGU, SADI, EADP) using a free variable for occupancy factor implemented in SHELXL [24]. The occupancy ratio for the main and second positions were 69/31 and 59/41, respectively. Crystallo-

Table 1. Crystal data, details of X-ray data collection and structure refinement parameters for compound **1**

Empirical formula	C ₉₂ H ₁₄₄ Cd ₄ N ₁₂ O ₄₄
Formula weight	2571.78
Temperature, K	100(2)
Crystal system, space group, <i>Z</i>	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁ , 2
<i>a</i> , <i>b</i> , <i>c</i> , Å	12.4904(2), 12.6121(2), 35.6802(5)
<i>V</i> , Å ³	5620.71
<i>D</i> _{calc} , Mg/m ³	1.520
μ , mm ⁻¹	0.837
<i>F</i> (000)	2648
Crystal size, mm	0.407 × 0.292 × 0.262
Radiation; λ , Å	MoK α ; 0.71073
θ , deg	1.713–27.441
<i>h</i> , <i>k</i> , <i>l</i> ranges	–16 ≤ <i>h</i> ≤ 16, –16 ≤ <i>k</i> ≤ 16, –46 ≤ <i>l</i> ≤ 46
Number of reflections: measured (<i>N</i> ₁)/ <i>R</i> _{int} , unique with <i>I</i> > 2 σ (<i>I</i>) (<i>N</i> ₂)	81463/0.0294, 12843
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	12843/325/828
<i>R</i> ₁ / <i>wR</i> ₂ relative to <i>N</i> ₁	0.0167/0.0382
<i>R</i> ₁ / <i>wR</i> ₂ relative to <i>N</i> ₂	0.0163/0.0381
<i>S</i>	1.052
Absolute structure parameter	–0.027(4)
$\Delta_{\min}/\Delta\rho_{\max}$, e Å ⁻³	–0.267/0.424

graphic data and refinement details for polymer **1** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under CCDC no. 2113022. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Synthesis

Using a simple approach of self-assembling solution reaction, equivalent amounts of Cd(NO₃)₂·4H₂O, itaconic acid (ita), and 1,2-bis(4-pyridyl)ethane (bmp) were mixed in a 50 : 50 water-methanol solution under ambient conditions. Slow evaporation of the solvents yielded translucent crystals of compound **1**. These crystals were insoluble in common solvents and air and moisture stable.

Crystal Structure

Polymer **1** crystallizes in the orthorhombic system with space group *P*2₁2₁2₁. The molecular structure of compound **1** consists of two crystallographically independent Cd centers, two ita ligands, three bmp ligands and one aqua ligand (Fig. 2). Remarkably, the distorted octahedral (Cd1) and distorted pentagonal bipyramidal (Cd2) coordination geometries coexist in the metal centers. Consequently, the Cd–O bond lengths vary from 2.2803(16) to 2.6321(17) Å, while the Cd–N distances range from 2.3008(19) to 2.341(2) Å, similar to values found in related Cd(II) complexes [11, 26, 27]. In the crystal structure of polymer **1**, two molecules {[Cd₂(H₂O)(ita)₂(bpe)₃]}·(H₂O)₁₃ are associated into a tetranuclear complex through hydrogen bonds formed mainly by the non-coordinated carboxylate oxygen (O2) atom and coordinated carboxylate oxygen atoms (O1, O3, O4, O5, O6, O7) of ita ligands and aqua ligand (O9), as well as their supramolecular interactions with crystallization water molecules (O10, O12, O13, O16, O17, O21, mainly) (Table 3), giving rise to secondary building units {[Cd₄(H₂O)₂(ita)₄(bpe)₆]}·(H₂O)₂₆ in compound **1**. This type of distinctive supramolecular binuclear and polynuclear structures, although rare, has been previously found in other coordination complexes and polymers [28]. Asymmetric units with more than one molecule (*Z'* > 1) are still considered oddities in crystallography, because there are few crystal structures with such characteristics [29]. It is considered that these high *Z'* structures imply high energy minima on the crystallization path to the final thermodynamic crystal [30]. Therefore, these types of dimers are stabilized due to intermolecular hydrogen bonds, which are promoted by lattice water molecules surrounding the complexes [31].

The 3D structure of compound **1** results from the existence of two different modes of coordination of the carboxylate moieties of the ita ligand with metal centres: monodentate and chelate bidentate in Cd1 and chelate bidentate in Cd2. More broadly, bpe also binds these metal centres in different ways: as a monoden-

Table 2. Selected bond lengths and angles for compound **1**

Bond	Length, Å	Bond	Length, Å
Cd(1)–O(1)	2.2803(16)	Cd(2)–N(5)	2.322(2)
Cd(1)–N(2)	2.3153(19)	Cd(2)–O(5)	2.3508(16)
Cd(1)–N(3)	2.335(5)	Cd(2)–O(9)	2.3876(16)
Cd(1)–N(6) ^{#1}	2.341(2)	Cd(2)–O(7) ^{#3}	2.3965(17)
Cd(1)–O(3) ^{#2}	2.3656(16)	Cd(2)–O(8) ^{#3}	2.4516(16)
Cd(1)–O(4) ^{#2}	2.4933(16)	Cd(2)–O(6)	2.6321(17)
Cd(2)–N(4)	2.3008(19)		
Bond	Angle, deg	Bond	Angle, deg
O(1)–Cd(1)–N(2)	88.76(6)	N(4)–Cd(2)–O(9)	81.43(6)
O(1)–Cd(1)–N(3)	87.2(2)	N(5)–Cd(2)–O(9)	93.46(6)
N(2)–Cd(1)–N(3)	98.78(13)	O(5)–Cd(2)–O(9)	86.84(6)
O(1)–Cd(1)–N(6) ^{#1}	96.84(7)	N(4)–Cd(2)–O(7) ^{#3}	94.59(7)
N(2)–Cd(1)–N(6) ^{#1}	174.37(7)	N(5)–Cd(2)–O(7) ^{#3}	88.54(6)
N(3)–Cd(1)–N(6) ^{#1}	80.98(12)	O(5)–Cd(2)–O(7) ^{#3}	163.10(6)
O(1)–Cd(1)–O(3) ^{#2}	132.05(6)	O(9)–Cd(2)–O(7) ^{#3}	77.29(6)
N(2)–Cd(1)–O(3) ^{#2}	88.90(6)	N(4)–Cd(2)–O(8) ^{#3}	89.20(6)
N(3)–Cd(1)–O(3) ^{#2}	140.4(2)	N(5)–Cd(2)–O(8) ^{#3}	97.47(6)
N(6) ^{#1} –Cd(1)–O(3) ^{#2}	87.77(6)	O(5)–Cd(2)–O(8) ^{#3}	142.71(6)
O(1)–Cd(1)–O(4) ^{#2}	172.62(5)	O(9)–Cd(2)–O(8) ^{#3}	129.53(6)
N(2)–Cd(1)–O(4) ^{#2}	87.14(6)	O(7) ^{#3} –Cd(2)–O(8) ^{#3}	54.05(6)
N(3)–Cd(1)–O(4) ^{#2}	87.4(2)	N(4)–Cd(2)–O(6)	93.91(6)
N(6) ^{#1} –Cd(1)–O(4) ^{#2}	87.22(6)	N(5)–Cd(2)–O(6)	87.06(6)
O(3) ^{#2} –Cd(1)–O(4) ^{#2}	54.04(5)	O(5)–Cd(2)–O(6)	52.32(5)
N(4)–Cd(2)–N(5)	173.25(7)	O(9)–Cd(2)–O(6)	139.10(5)
N(4)–Cd(2)–O(5)	88.67(6)	O(7) ^{#3} –Cd(2)–O(6)	143.54(5)
N(5)–Cd(2)–O(5)	86.65(6)	O(8) ^{#3} –Cd(2)–O(6)	90.73(5)

Symmetry codes: ^{#1} $-x + 2, y + 3/2, -z + 1/2$; ^{#2} $x - 1/2, -y + 5/2, -z + 1$; ^{#3} $-x + 2, y + 1/2, -z + 1/2$.

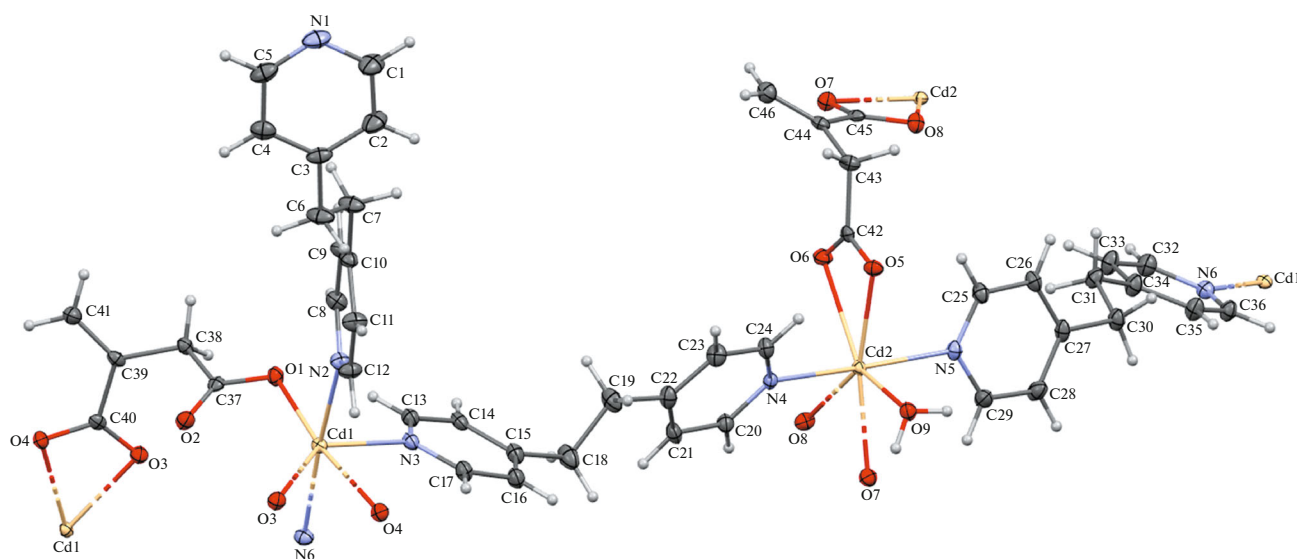


Fig. 2. Molecular structure of compound **1**. Ellipsoids are drawn with a 60% probability. Crystalline water molecules have been omitted for clarity.

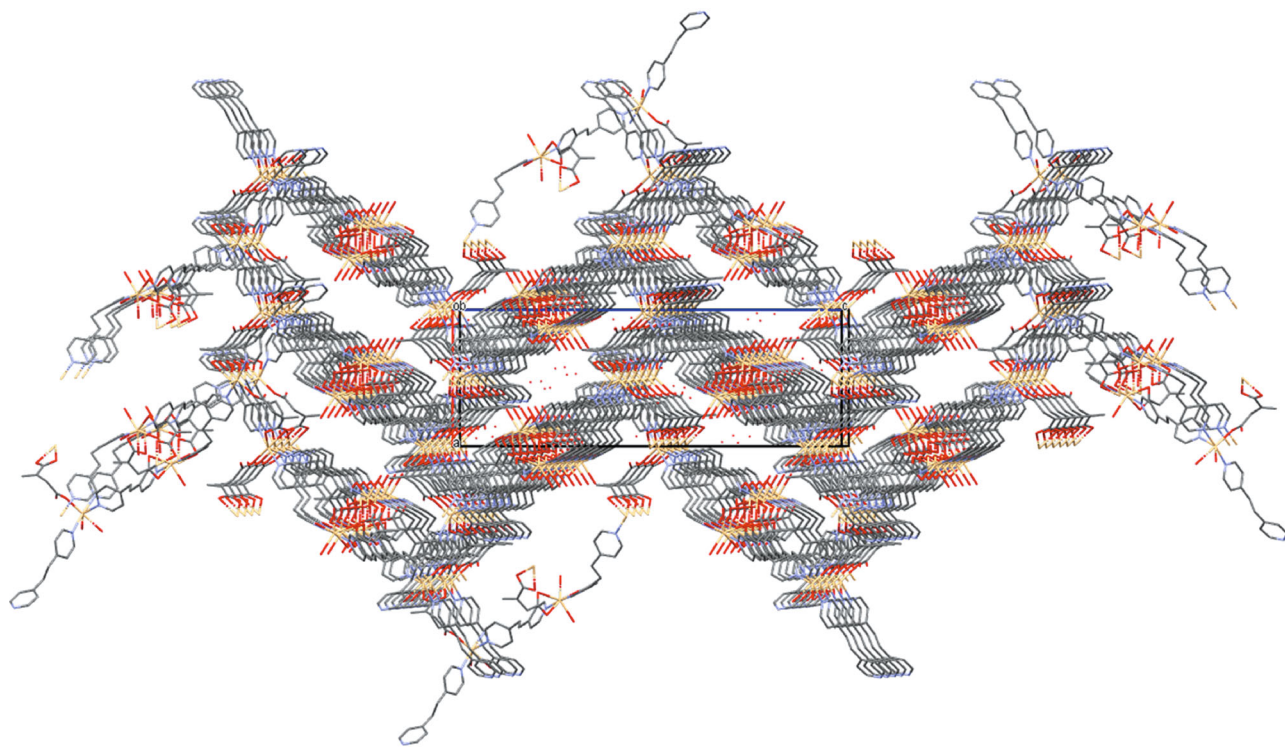


Fig. 3. Packing structure showing a 3D array in compound **1**. Hydrogen atoms have been omitted for clarity.

tate ligand in Cd1 and as a common bridging ligand in Cd2 (Fig. 3). Hence, the resulting new topology of crystal **1**, according to the analysis performed by ToposPro [32], consists of a 4,4-*c* net with the point symbol $\{5 \cdot 8^5\}\{5^3 \cdot 6^2 \cdot 8\}$ (Fig. 4).

CONCLUSIONS

A novel three-dimensional cadmium coordination polymer has been designed and synthesized under ambient conditions using the bridging ligands itaconate and 1,2-bis(4-pyridyl)ethane. Polymer **1** has two

Table 3. Hydrogen bonds in compound **1**

$D-H\cdots A$	$d(D-H)$, Å	$d(H\cdots A)$, Å	$d(D\cdots A)$, Å	$\angle(DHA)$, deg
O(9)–H(9A)···O(21) ^{#3}	0.839(13)	2.031(14)	2.864(3)	172(3)
O(9)–H(9B)···N(1) ^{#7}	0.837(13)	1.842(14)	2.669(3)	169(3)
O(13)–H(13A)···O(1)	0.838(13)	1.977(15)	2.805(3)	169(3)
O(13)–H(13B)···O(15) ^{#8}	0.828(13)	2.009(17)	2.804(3)	160(3)
O(19)–H(19T)···O(20) ^{#9}	0.77(4)	2.13(4)	2.900(3)	172(3)
O(19)–H(19S)···O(8) ^{#10}	0.77(3)	2.04(4)	2.803(3)	170(4)
O(20)–H(20A)···O(21)	0.833(13)	2.066(14)	2.867(3)	161(3)
O(20)–H(20B)···O(6)	0.841(13)	2.049(15)	2.861(2)	162(3)
O(21)–H(21A)···O(22)	0.842(13)	1.953(14)	2.784(3)	169(3)
O(21)–H(21B)···O(4) ^{#8}	0.834(13)	2.261(18)	3.028(2)	153(3)
O(11)–H(11A)···O(7) ^{#11}	0.832(13)	2.032(15)	2.855(2)	170(3)
O(11)–H(11B)···O(10)	0.833(13)	2.044(19)	2.819(3)	155(3)
O(18)–H(18E)···O(19)	0.840(13)	1.892(14)	2.728(3)	174(3)
O(18)–H(18F)···O(17)	0.845(13)	1.884(14)	2.724(3)	173(3)
O(15)–H(15A)···O(12) ^{#11}	0.831(13)	1.950(14)	2.778(3)	174(3)
O(15)–H(15B)···O(14)	0.841(13)	1.877(15)	2.711(3)	171(3)
O(16)–H(16A)···O(18) ^{#12}	0.837(13)	1.982(15)	2.809(3)	170(3)
O(16)–H(16B)···O(5)	0.844(13)	1.887(14)	2.716(2)	167(2)
O(17)–H(17A)···O(16)	0.828(12)	1.960(14)	2.757(3)	161(3)
O(17)–H(17B)···O(9)	0.846(13)	1.974(14)	2.814(2)	172(3)
O(10)–H(10A)···O(20) ^{#11}	0.829(13)	2.255(14)	3.068(3)	167(3)
O(10)–H(10B)···O(2)	0.841(13)	1.872(15)	2.684(2)	162(3)
O(12)–H(12A)···O(3)	0.829(13)	1.996(13)	2.824(2)	176(3)
O(12)–H(12B)···O(10) ^{#4}	0.831(13)	2.155(13)	2.986(3)	178(3)
O(14)–H(14A)···O(11) ^{#13}	0.835(13)	2.013(13)	2.847(3)	177(3)
O(14)–H(14B)···O(13)	0.835(13)	1.925(14)	2.747(3)	168(3)
O(22)–H(22A)···O(16) ^{#14}	0.844(13)	2.008(15)	2.838(3)	168(3)
O(22)–H(22B)···O(18) ^{#14}	0.850(13)	2.123(15)	2.963(3)	169(3)

Symmetry codes: ^{#3} $-x + 2, y + 1/2, -z + 1/2$; ^{#4} $x + 1/2, -y + 5/2, -z + 1$; ^{#7} $-x + 1/2, -y + 1, z - 1/2$; ^{#8} $x + 1/2, -y + 3/2, -z + 1$; ^{#9} $x - 1, y, z$; ^{#10} $-x + 1, y + 1/2, -z + 1/2$; ^{#11} $x - 1/2, -y + 3/2, -z + 1$; ^{#12} $-x + 1, y - 1/2, -z + 1/2$; ^{#13} $x, y - 1, z$; ^{#14} $x + 1, y, z$.

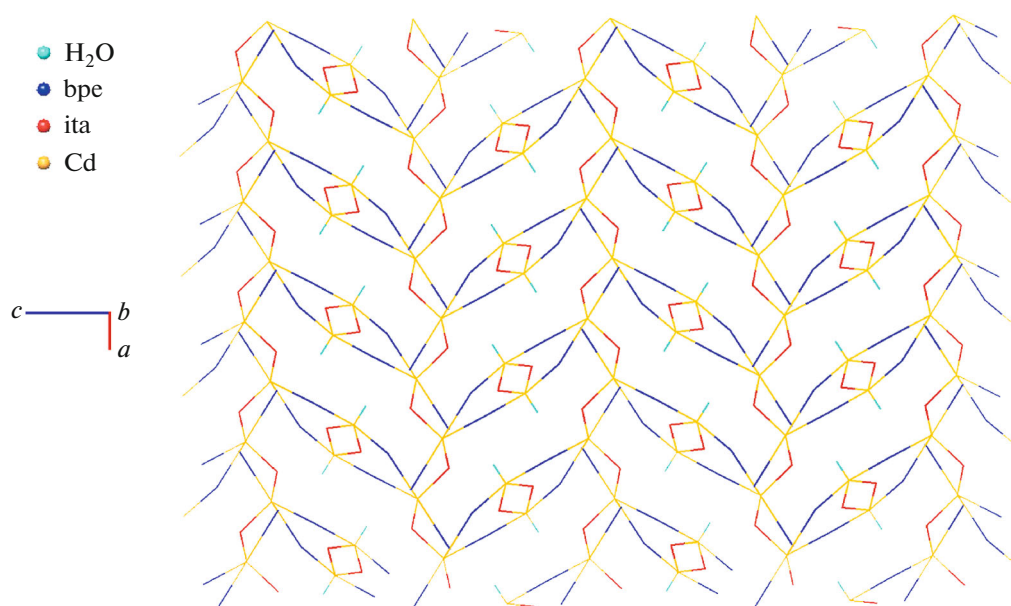


Fig. 4. Simplified topological network of polymer 1.

crystallographically independent Cd centers exhibiting distorted octahedral and distorted pentagonal bipyramidal coordination geometries. The secondary building units of compound **1** contain four metal centers resulting from supramolecular hydrogen bonds of the ita ligand oxygen atoms with crystallization water molecules. Coordination polymer **1** displays a new 3D topology.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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