Dokuz Eylül Üniversitesi Mühendislik Fakültesi Fen ve Mühendislik Dergisi
Dokuz Eylul University Faculty of Engineering Journal of Science and Engineering

Basılı/Printed ISSN: 1302-9304. Elektronik/Online ISSN: 2547-958X

Syntheses and Characterizations of Zinc(II) and Cadmium (II) Coordination Polymers with 1,4-bis ((1H-1,2,4-triazol-1-yl)methyl)benzene

1,4-Bis((1H-1,2,4-triazol-1-il)metil)benzen ile Çinko(II) ve Kadmiyum(II) Koordinasyon Polimerlerinin Sentezi ve Karakterizasyonu

Pelin Köse Yaman [1,2*], Hakan Erer [2], Okan Zafer Yeşilel [2]

[1] Dokuz Eylül University, Faculty of Sciences, Department of Chemistry, 35390, İzmir, TURKEY
[2] Eskişehir Osmangazi University, Faculty of Science and Letters, Department of Chemistry, 26480, Eskişehir, TURKEY
*Sorumlu Yazar / Corresponding Author **: pelin.kose@deu.edu.tr

Geliş Tarihi / Received: 17.07.2019 *Araştırma Makalesi/Research Article*
Kabul Tarihi / Accepted: 14.10.2019 *DOI: 10.21205/deufmd.2020226511*
Atıf şekli/ How to cite: KOSE,YAMAN, P., ERER, H., YESILEL, O.Z.(2020). Syntheses and Characterizations of Zinc(II) and Cadmium(II) Coordination Polymers with 1,4-bis ((1H-1,2,4-triazol-1-yl)methyl)benzene. DEUFMD, 22(65), 425-435.

Abstract

Two Zinc(II) and Cadmium(II) coordination polymers, namely $[ZnCl_2(\mu\text{-ptmb})]_n$ (**1**) and $[Cd(\mu_4\text{-}SO_4)(\mu\text{-ptmb})]_n$ (**2**) have been obtained with hydrothermal method at 120°C based on flexible ligand 1,4-bis((1H-1,2,4-triazol-1-yl)methyl)benzene (ptmb) in this study. The single-crystal X-ray analyses indicate that complexes **1** and **2** crystallize in the triclinic with P-1 space group and the orthorhombic crystal system with space group Pccn, respectively. In **1**, Zn(II) ions display a tetrahedral geometry with two chloride and two ptmb ligands. The ptmb ligand acts to bridge neighboring Zn(II) centres into a 1D zig-zag polymeric chain structures. In **2**, Cd(II) ions display octahedral geometry with two ptmb and four different sulfato ligands. Four contiguous Cd(II) ions are bridged through the agency of four sulfato ligands to form a 2D layer. Two adjacent 2D layers further extended into a 3D structure through the bridging ptmb ligands. Besides, the thermal properties of synthesized new complexes have been investigated.

Keywords: *1,4-bis((1H-1,2,4-triazol-1-yl)methyl)benzene, Zinc (II) complex, Cadmium (II) complex, Coordination polymers, Hydrothermal Synthesis.*

Öz

Bu çalışmada esnek 1,4-bis((1H-1,2,4-triazol-1-yl)metil)benzen (ptmb) ligandı esas alınarak 120°C de hidrotermal sentez yöntemiyle $[ZnCl_2(\mu\text{-ptmb})]_n$ (1) ve $[Cd(\mu_4\text{-}SO_4)(\mu\text{-ptmb})]_n$ (2) kapalı formülüne sahip iki yeni Çinko(II) ve Kadmiyum(II) koordinasyon polimeri sentezlenmiştir. X-ışınları tek kristal analiz sonuçlarına göre 1 ve 2 kompleksi sırasıyla P-1 uzay grubu ile triklinik ve Pccn uzay grubu ile ortorombik kristal sisteminde kristallenmişlerdir. **1** de Zn(II) iyonları iki ptmb ligandı ve iki klor ile tetrahedral geometri göstermiştir. Ptmb ligandı komşu Zn(II) merkezleri arasında köprü rolü oynayarak 1D zig-zag polimerik zincir yapılar oluşturmuştur. **2**, de Cd(II) iyonları iki ptmb ve dört farklı sülfat ligandı ile oktahedral geometri sergilemiştir. Dört bitişik Cd(II) iyonları 2D tabaka oluşturmak için dört sülfat ligandı ile köprülenmiştir. 2D tabakalar köprü ptmb ligandı sayesinde 3D kafes yapıya genişler. Ayrıca, yeni komplekslerin termal özellikleri incelenmiştir.

Anahtar Kelimeler: *1,4-bis((1H-1,2,4-triazol-1-yl)metil)benzen, Kadmiyum (II) kompleks, Çinko (II) kompleks, Koordinasyon polimeri, Hidrotermal Sentez.*

1. Introduction

Recently, the designed synthesis of novel coordination polymers (NCPs) has charming due to not only their attracting diversity of architectural but also potential applications of NCPs in varieties areas (for example; adsorption, drug delivery, magnetism, luminescence and catalysis etc.) [1–4]. The metal ions and organic bridging ligands build numerous one-, two-, and three- dimensional polymeric networks with this type of coordination polymer synthesis. [5,6]. In the coordination polymers synthesis, the choice of cluster subunits like organic linkers and metal ions is of very important because it leads to a variety of unusual shapes polymeric frameworks with large gaps, and novel properties [7,8]. Besides the construction of the building units, the network architecture can also rely on the choice of the molar ratios of the molecular components, temperature, pH and solvent [9–11].

The ptmb ligand has remarkable capacities as a ligand for the generation of coordination polymers: It is flexibly N-bridging ligand which has two triazole rings and can freely rotate along the -CH_2-[12]. In addition, this ligand adopts some form of compatibility with respect to constraints due to the binding geometry of metal ions [13]. It is aforethought an appealing type of flexible organic ligand for coordination polymers. [7–9].

In this article, we have investigated the influence of the flexible ligand ptmb with different metal salts Zinc(II) and Cadmium(II). Two new coordination polymers $[ZnCl_2(\mu\text{- ptmb})]_n$ (**1**) and $[Cd(\mu_4\text{-}SO_4)(\mu\text{-ptmb})]_n$ (**2**) were obtained with the hydrothermal method. The ptmb ligands serve as linker to connect subunits giving rise to 1D structure for **1** and 3D networks for **2**.

2. Material and Method

Elemental analyses (C, H, and N) were performed on a Perkin Elmer 2400C Elemental Analyzer. FT-IR spectra of the complexes were taken with Perkin-Elmer FT-IR 100 spectrometer in the region of 4000–400 cm^{-1} using KBr pellet method. Thermal analyses were carried out in the temperature range 30–1000 °C in a nitrogen atmosphere with platinum crucible on a Perkin Elmer Diamond TG/DTA thermal analyzer.

2.1 Crystallographic analyses

The single crystal X-Ray diffraction data of **1** and **2** were selected on a Bruker D8 QUEST diffractometer at 296 K with Mo-Kα radiation. The structures were solved by SHELXT and refined by full-matrix least-squares on all F2 data using SHELXL in conjunction with the OLEX2 graphical user interface [17,18]. For all complexes, the anisotropic thermal parameters were refined for non-hydrogen atoms and hydrogen atoms were calculated and refined with a riding model. Molecule drawings were carried out with Mercury and OLEX2 programs [19]. The crystallographic information file was deposited with the Cambridge Crystallographic Data Centre (CCDC) with the reference number **1917250** for **1** and **1917251** for **2**. The details of data collection and crystal structure determinations are given in Table 1.

2.2 Synthesis of $[ZnCl_2(\mu\text{-ptmb})]_n$ (1):

A mixture of $ZnCl_2$ (27.26 mg, 0.2 mmol), ptmb (48.0 mg, 0.2 mmol), in H_2O (10 mL) stirred for 40 minutes at 80 °C. Then the solution was sealed in a 25 mL glass vial and directly heated to 120 °C for 3 days. The glass vial cooled to 25°C. Colorless single crystals were obtained with a 48% yield. For complex $C_{12}H_{12}Cl_2N_6Zn$ (376.55 g/mol) Anal. Calc.: C, 38.28; H, 3.21; N, 22.32. Found: C, 38.01; H, 3.26; N, 22.53%. IR (KBr)/cm^{-1}: 3118s, 1531s, 1278s, 1128s, 999w, 737s.

2.3 Synthesis of $[Cd(\mu_4\text{-}SO_4)(\mu\text{-ptmb})]_n$ (2):

The synthetic procedure for **2** was similar to that for **1** except that $CdSO_4{\cdot}8/3H_2O$ (51.31 mg, 0.2 mmol) was used instead of $ZnCl_2$. For complex $C_{12}H_{12}N_6O_4SCd$ (448.74 g/mol) Anal. Calc.: C, 32.12; H, 2.70; N, 18.73. Found: C, 32.94; H, 2.88; N, 18.96%. IR (KBr)/cm^{-1}: 3118 s, 1520 s, 1275 s, 1098 s, 1008 s, 736 s.

3. Results

The main crystal data together with generation parameters details are summarized in Table 1. Further, other selected properties of crystals (the bond lengths and the angles) are shown in Table 2 and 3.

3.1 FT-IR spectra:

The IR spectra of free ligands and compounds **1-2** were analysed as KBr pellets in the range 4000-400 cm^{-1}. In the high energy range, 3139 and 3123 cm^{-1} absorption peaks originate from ν(C-H) stretches for **1** and **2**, respectively.

The absorption peaks of 1531 and 1520 cm^{-1} are assigned to the stretching C=N in triazole ring vibrations of the ptmb ligand in **1** and **2** respectively, which exhibit certain shifts in contrast with 1510 cm^{-1} in ligand[20].

In the finger print range, 1275-1278cm^{-1}, 1128-1098cm^{-1}, 999-1008 cm^{-1} absorption peaks may originate from ν(C-C), ν(C-N) stretches for **1** and **2** respectively. The absorption bands at 728 and 736 cm^{-1} are attributed to benzene ring vibrations **1** and **2** respectively.

3.2 Structure description of $[ZnCl_2(\mu\text{-ptmb})]_n$ (1):

Single-crystal X-ray diffraction analysis exhibits that **1** forms crystal in the triclinic system with *P*-1 space group. The asymmetric unit of **1** consists of one Zn(II) ion, two chloride ligands, and two half different ptmb ligands. The Zn(II) ion is four-coordinated by two chloride ligands and two nitrogen atoms of two different ptmb ligands and display a tetrahedral geometry (τ_4=0.911)[21](Figure 1.).

The Zn-Cl/N bond lengths vary from 2.043(2) to 2.2363(8) Å, which are in accordance with similarly reported complexes [22]. Two Zn(II) ions are bridged by nitrogen atoms of two ptmb ligands to form a 1D zig-zag polymeric chain structure (Figure 2.). The ptmb ligands display an angular exo-bidentate bridging coordination mode with the intertriazol dihedral angles of 180° (through N1–N3–$N3^{ii}$–$N1^{ii}$) and -180° (through N6–N4–$N4^{i}$–$N6^{i}$). The distances between the Zn(II) ions bridged by the ptmb ligands are 15.222 Å and 15.148 Å. The neighboring 1D polymeric chain structures are further connected by through C-H···Cl interactions (Figure 3.) to construct 3D supramolecular networks (Figure 4.).

Table 1. Crystal data and structural refinement parameters for complexes **1** and **2.**

	1	**2**
Formula	$C_{12}H_{12}Cl_2N_6Zn$	$C_{12}H_{12}N_6O_4SCd$
Formula weight	376.55	448.74
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1	*P*ccn
a **(Å)**	8.7070 (12)	30.091 (6)
b **(Å)**	9.0931 (13)	4.7388 (10)
c **(Å)**	10.7750 (16)	9.8346 (19)
α(°)	88.083 (5)	90
β **(°)**	83.739 (5)	90
γ(°)	61.725 (4)	90
V **(Å³)**	746.67 (19)	1402.4 (5)
Z	2	4
D_c **(g cm⁻³)**	1.675	2.125
μ (mm⁻¹)	2.00	1.74
θ range (°)	3.1–28.3	3.4–28.3
Measured refls.	38836	20072
Independent	3717	1733
R_{int}	0.049	0.049
S	1.03	1.12
$R[F^2 > 2\sigma(F^2)]$ /	0.036/0.073	0.043/0.107
$\Delta\rho_{max}/\Delta\rho_{min}$ **(eÅ⁻³)**	0.45/−0.45	0.66/−1.62

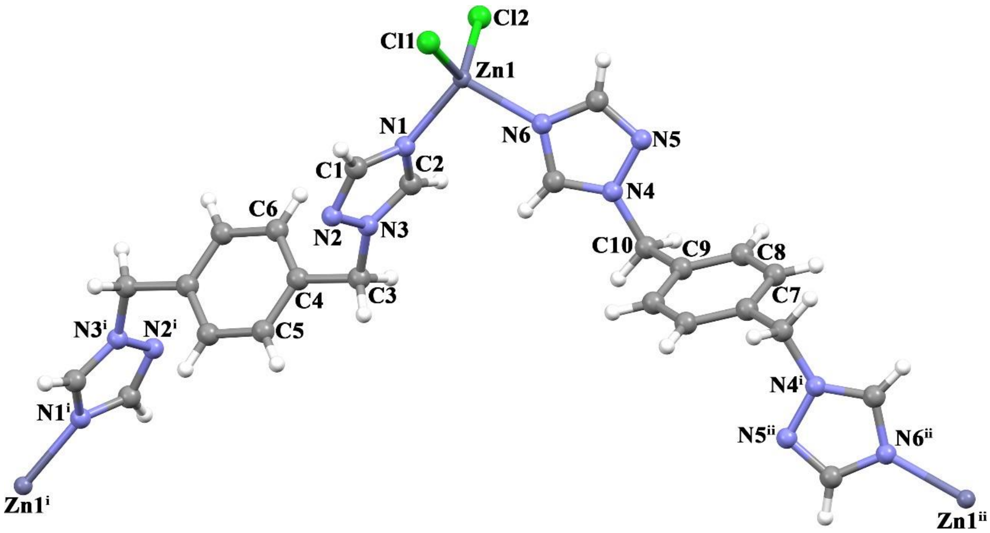

Figure 1. The view of the crystal structure for **1**

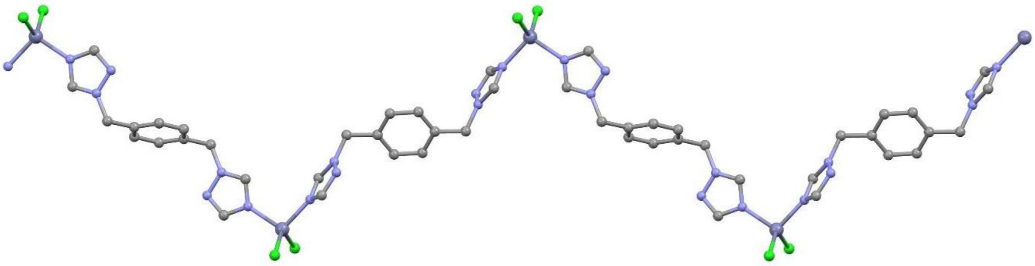

Figure 2. The view of a 1D zigzag chain of **1**

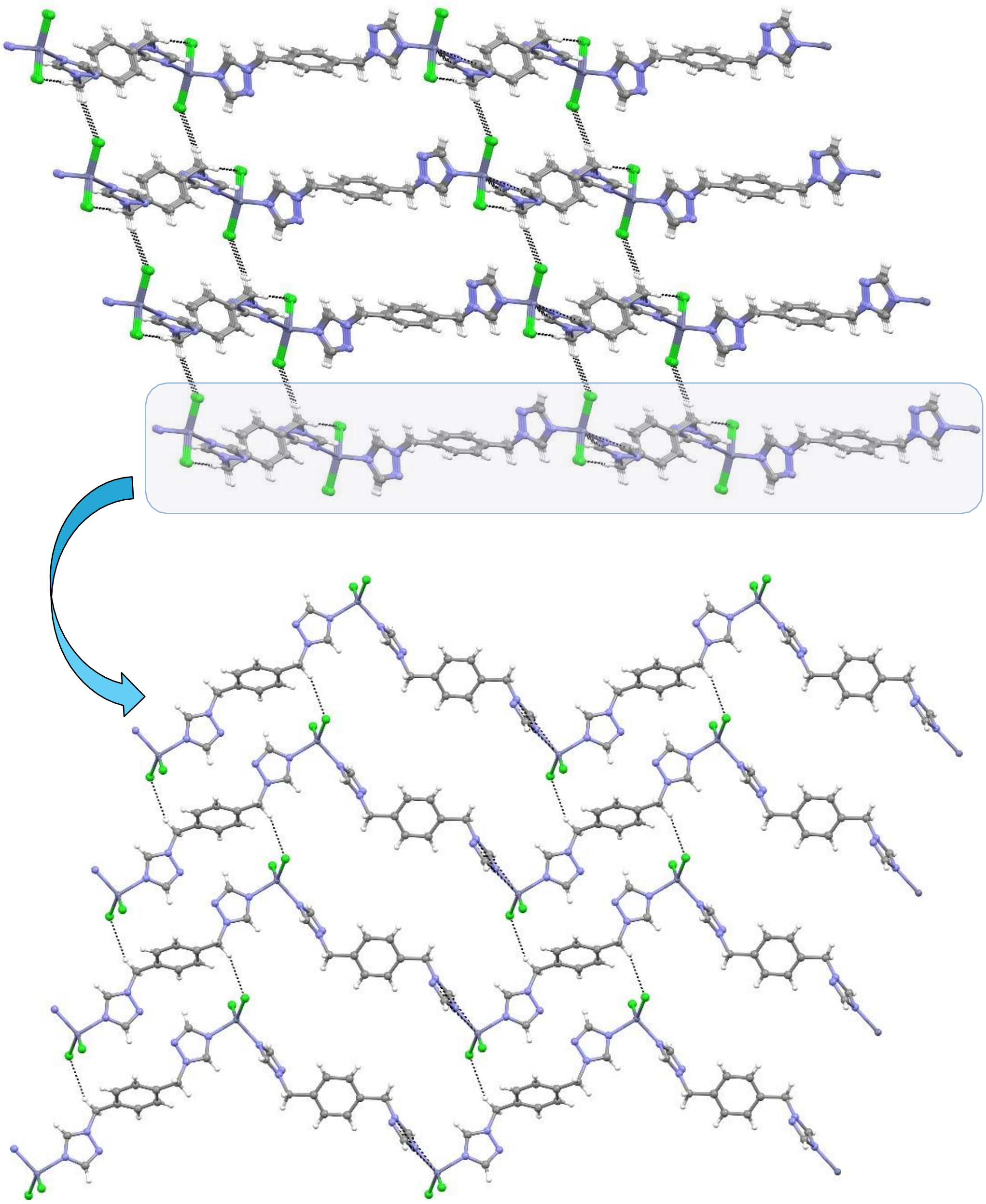

Figure 3. A view of the C-H···Cl interactions to construct 3D supramolecular networks in **1**

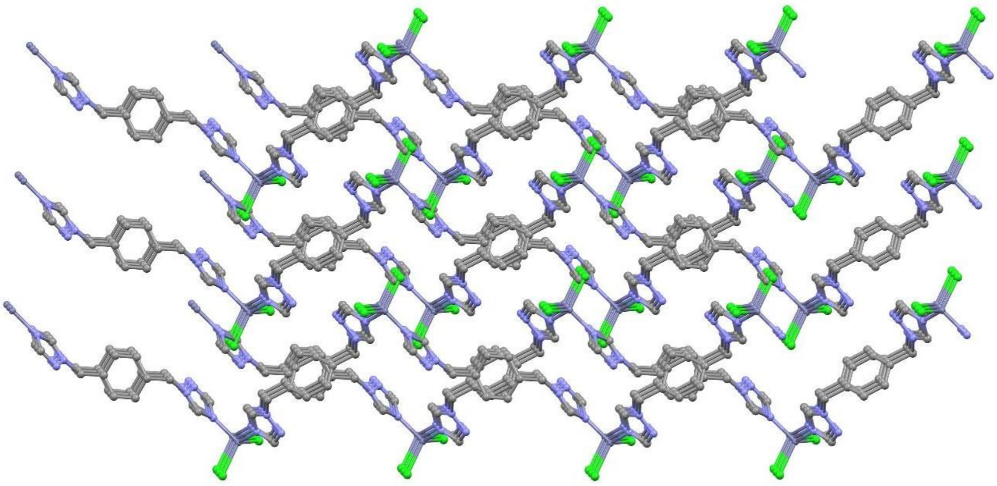

Figure 4. 3D supramolecular structure of **1**

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

Bond Lengths (Å)			
Zn1–Cl2	2.2363 (8)	Zn1–N1	2.043 (2)
Zn1–Cl1	2.2069 (8)	Zn1–N6	2.043 (2)
Angles (°)			
Cl1–Zn1–Cl2	120.69 (3)	N1–Zn1–N6	102.38 (9)
N1–Zn1–Cl2	109.38 (7)	N6–Zn1–Cl2	104.44 (7)
N1–Zn1–Cl1	107.59 (7)	N6–Zn1–Cl1	110.86 (7)

*Symmetry codes: (i) −x, −y+1, −z; (ii) −x+1, −y, −z+2.

3.3 Structure description of [Cd(μ_4-SO_4)(μ-ptmb)]$_n$ (2):

Single-crystal X-ray analysis reveals that **2** forms crystals in a orthorhombic crystal system with space group *P*ccn. The asymmetric unit of **2** contains a half of Cd(II) ion, a half of sulfato and a half of ptmb ligands. As shown in Figure 5., the Cd(II) ion is six-coordinated, which is completed by four oxygen atoms from four different sulfato ligands occupying equatorial plane [Cd1−O1 = 2.327(3); Cd1−O1^{i} = 2.327(3); Cd1−O2^{ii} = 2.408(3); Cd1−O2^{iii} = 2.408(3) Å] and two nitrogen atoms from two ptmb ligands occupying the axial site [Cd1−N1 = 2.327(4); Cd1−N1^{i} = 2.327(4) Å]. The Cd-O bond distances range between 2.327(3)-2.408(3) Å similar to those found in [$Cd_3(C_8H_5N_2O_2)_2(\mu_4$-$SO_4)(\mu_5$-$SO_4)(H_2O)_3]_n$ (2.301(3)-2.437(3) Å) [23] and [$Cd_2(\mu_3$-$SO_4)(\mu_4$-$SO_4)(C_{13}H_8N_4)(H_2O)_2]_n$ (2.2408(18)-2.4782(18) Å) [24]. The sulfato ligands coordinates to the metal centre through the μ_4-η^1:η^1:η^1:η^1 coordination mode [25]. Four Cd(II) ions are bridged by oxygen atoms of four sulfato ligands to form 2D layer structure (Figure 6.). The adjacent 2D Cd-SO_4 layers are connected by the exobidentate ptmb ligands to further extend a 3D framework (Figure 7.). The ptmb ligands display an angular exo-bidentate bridging coordination mode with the intertriazol dihedral angles of - 180° (through N1–N3–N3^{vi}–N1^{vi}). The distance between the Cd(II) ions bridged by the ptmb ligand is 15.411 Å.

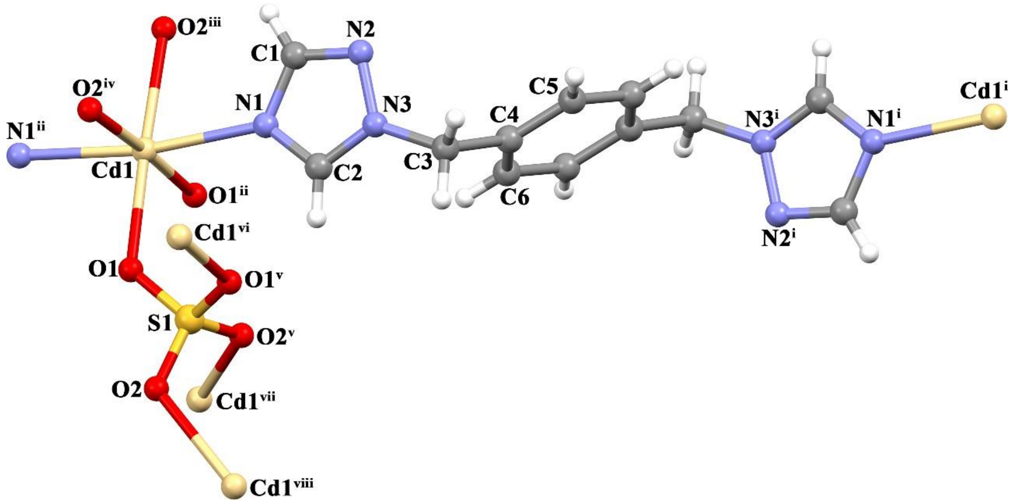

Figure 5. View of the crystal structure for **2**

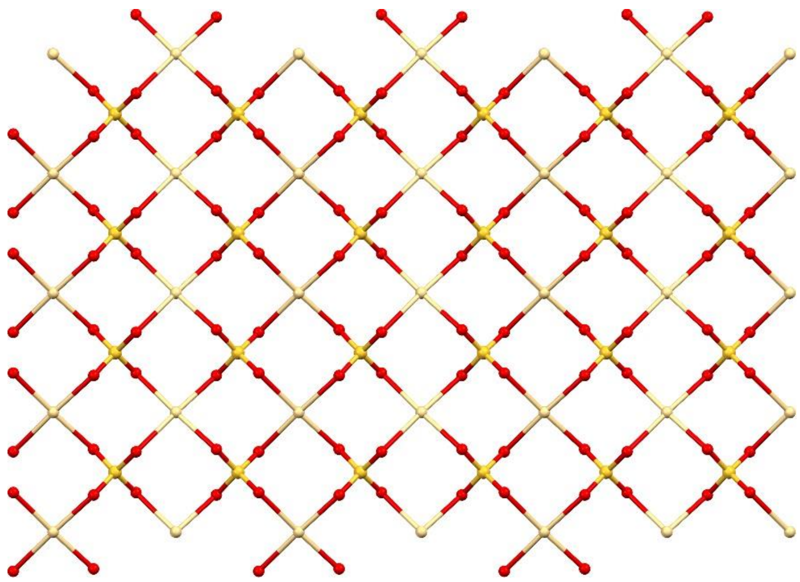

Figure 6. A view of the 2D Cd-SO_4 layer in **2**.

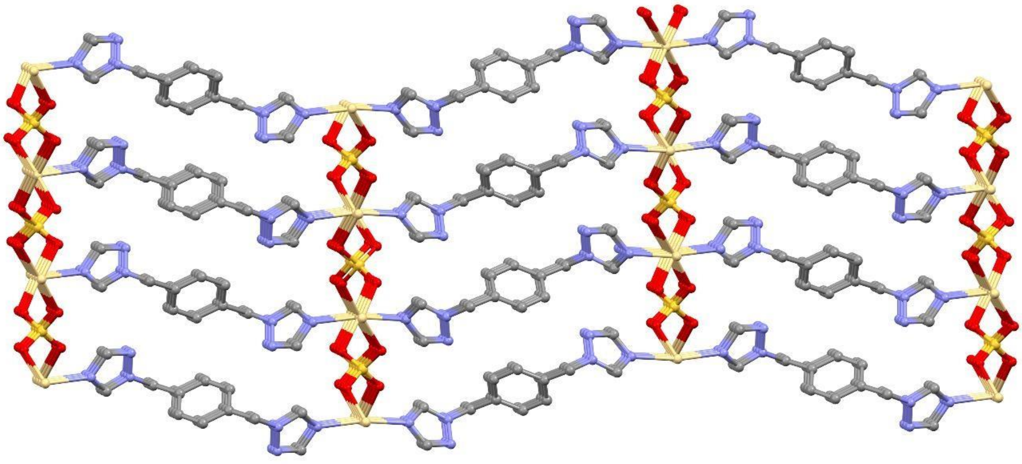

Figure 7. A view of a 3D framework of **2**

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

Bond Lengths (Å)			
Cd1–O1	2.327 (3)	Cd1–O2^{iii}	2.408 (3)
Cd1–O1^{i}	2.327 (3)	Cd1–N1^{i}	2.327 (4)
Cd1–O2^{ii}	2.408 (3)	Cd1–N1	2.327 (4)
Angles (°)			
O1–Cd1–O1^{i}	91.55 (17)	N1^{i}–Cd1–O1^{i}	100.56 (13)
O1^{i}–Cd1–O2^{ii}	177.03 (11)	N1–Cd1–O1^{i}	86.15 (13)
O1–Cd1–O2^{iii}	177.03 (11)	N1–Cd1–O2^{ii}	95.50 (12)
O1^{i}–Cd1–O2^{iii}	85.73 (12)	N1^{i}–Cd1–O2^{ii}	78.11 (13)
O1–Cd1–O2^{ii}	85.73 (12)	N1–Cd1–O2^{iii}	78.11 (13)
O1–Cd1–N1^{i}	86.15 (13)	N1^{i}–Cd1–O2^{iii}	95.50 (12)
O1–Cd1–N1	100.55 (13)	N1^{i}–Cd1–N1	170.46 (19)
O2^{iii}–Cd1–O2^{ii}	97.02 (16)		

*Symmetry codes: (i) −x+1/2, −y+3/2, z; (ii) x, −y+1/2, z+1/2; (iii) −x+1/2, y+1, z+1/2; (iv) −x+1/2, −y+1/2, z; (v) x, −y+1/2, z−1/2; (vi) −x+1, −y+1, −z+1

3.4 Thermal analysis of 1 and 2:

The TG, DTG, and DTA analysis were performed in a nitrogen atmosphere the range 30-1000°C (Figure 8 and 9.). Zn(II) complex is stable up to 326 °C. Cd(II) complex is much less stable and does not lose any weight until 304°C. Both complexes are collapsed in the thermal decomposition stages.

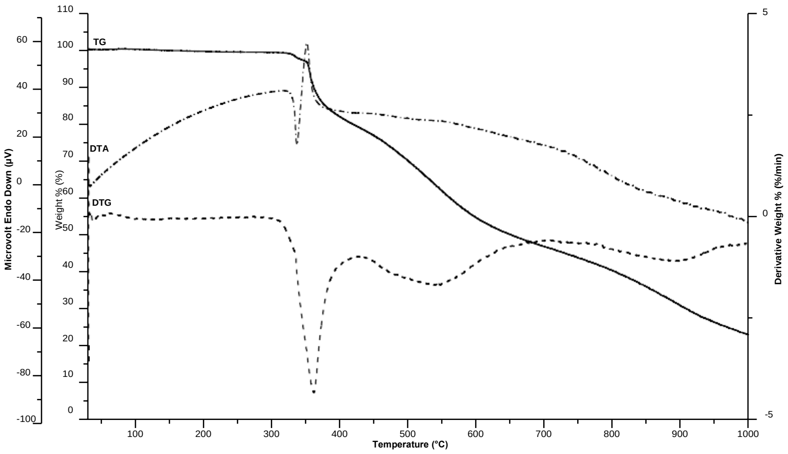

Figure 8. TG, DTG, and DTA curves of **1**

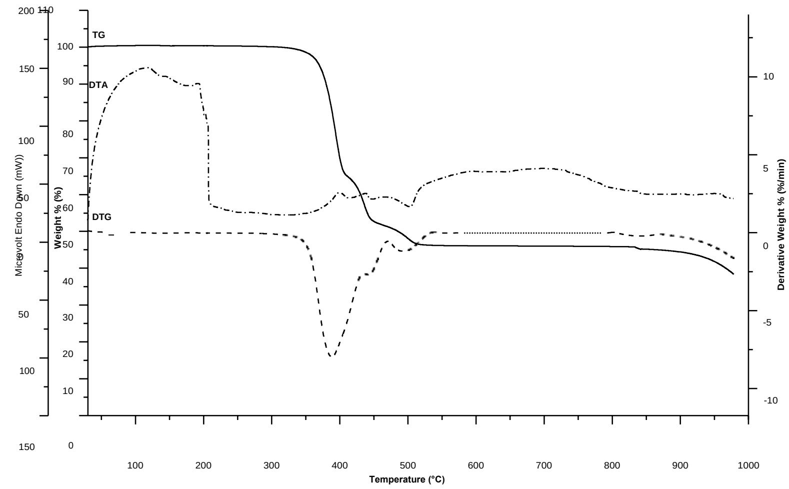

Figure 9. TG, DTG, and DTA curves of **2**

4. Discussion and Conclusion

In summary, a one- and three-dimensional coordination polymers have been successfully synthesized under hydrothermal reaction by using sulfato and 1,4-bis((1H-1,2,4-triazol-1-yl)methyl)benzene (ptmb) as bridging ligands. Complex **1** shows new 1D structure constructed from zinc(II) centres joined by ptmb linker. Complex **2** shows new 3D structure constructed from 2D Cd-SO_4 layer motifs joined by ptmb linker. These results show that the selection of metal salt and organic linkers plays a significant role in the dimensionality of desired NCPs.

Acknowledgment

The authors acknowledge to Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

References

[1] H. Huang, W. Gao, F. Liu, X.M. Zhang, J.P. Liu, Four 3D Mn(II) coordination polymers with diverse carboxylate-bridged magnetic chains: Syntheses, crystal structures, magnetic properties, Inorganica Chim. Acta. 484 (2019) 414–423. doi:10.1016/j.ica.2018.09.060.

[2] J.J. Perry IV, C.A. Bauer, M.D. Allendorf, Luminescent Metal-Organic Frameworks, Met. Fram. Appl. from Catal. to Gas Storage. (2011) 267–308. doi:10.1002/9783527635856.ch12.

[3] J.-Q. Liu, X.-F. Li, C.-Y. Gu, J.C.S. da Silva, A.L. Barros, S. Alves-Jr, B.-H. Li, F. Ren, S.R. Batten, T.A. Soares, A combined experimental and computational study of novel nanocage-based metal–organic frameworks for drug delivery, Dalt. Trans. 44 (2015) 19370–19382. doi:10.1039/C5DT02171E.

[4] B. Bhattacharya, R. Dey, P. Pachfule, R. Banerjee, D. Ghoshal, Four 3D Cd(II)-based metal organic hybrids with different N,N???-donor spacers: Syntheses, characterizations, and selective gas adsorption properties, Cryst. Growth Des. 13 (2013) 731–739. doi:10.1021/cg3014464.

[5] Y. Zhao, K. Li, J. Li, Solvothermal synthesis of multifunctional coordination polymers, Zeitschrift Fur Naturforsch. - Sect. B J. Chem. Sci. 65 (2010) 976–998.

[6] S. Kitagawa, R. Kitaura, S.I. Noro, Functional porous coordination polymers, Angew. Chemie - Int. Ed. 43 (2004) 2334–2375. doi:10.1002/anie.200300610.

[7] S. Kitagawa, R. Kitaura, S. Noro, Functional Porous Coordination Polymers, Angew. Chemie Int. Ed. 43 (2004) 2334–2375. doi:10.1002/anie.200300610.

[8] C. Shi, Z. Wang, Y. Chen, X. Zhang, Y. Zhao, Y. Tao, H. Wu, Structural diversity of four coordination polymers based on 5-nitro- 1,2,3-benzenetricarboxylic acid (H3nbta): Solvothermal syntheses, structural characterizations and properties, J. Solid State Chem. 253 (2017) 35–42. doi:10.1016/j.jssc.2017.05.010.

[9] L. Dobrzańska, D.J. Kleinhans, L.J. Barbour, Influence of the metal-to-ligand ratio on the formation of metal organic complexes, New J. Chem. 32 (2008) 813. doi:10.1039/b800720a.

[10] P. Köse Yaman, O.Z. Yeşilel, Hydrothermal synthesis and characterization of cobalt(II), nickel(II) and zinc(II) coordination polymers with 2,2′-dimethylglutarate and 1,2-bis(4-pyridyl)ethane, Polyhedron. 148 (2018) 189–194. doi:10.1016/j.poly.2018.04.006.

[11] F. Semerci, Effect of substituent groups on the structures of two semi-flexible bis (imidazole) directed Zn (II) -5- sulfoisophthalate coordination polymers : Syntheses , structures and photoluminescent properties, Polyhedron. 139 (2018) 73–79. doi:10.1016/j.poly.2017.09.049.

[12] X.J. Xu, Crystal Structure and Magnetic Property of a New Two-Dimensional Coordination Polymer Constructed By 1,4-Bis(1,2,4-Triazol-1-Ylmethyl)-Benzene and 4,4′-Sulfonyldibenzoic Acid, J. Struct. Chem. 56 (2015) 1008–1012. doi:10.1134/S0022476615050285.

[13] S.Y. Zhang, Z.J. Zhang, W. Shi, B. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Structural evolution and magnetic properties of CoIIcoordination polymers varied from 1D to 3D constructed by 1,4-bis(1,2,4-triazol- 1-ylmethyl)benzene, Dalt. Trans. 40 (2011) 7993–8002. doi:10.1039/c1dt10282f.

[14] X. Meng, Y. Song, H. Hou, H. Han, B. Xiao, Y. Fan, Y. Zhu, Hydrothermal syntheses, crystal structures, and characteristics of a series of Cd-btx coordination polymers (btx = 1,4-bis(triazol-1-ylmethyl)benzene), Inorg. Chem. 43 (2004) 3528–3536. doi:10.1021/ic0354670.

[15] B. Ding, H.A. Zou, Poly[bis[??-1,4-bis-(1,2,4-triazol1ylmeth-yl)benzene-??2 N4:N4???]dichloridomanganese(II)], Acta Crystallogr. Sect. E Struct. Reports Online. 66 (2010). doi:10.1107/S1600536810026322.

[16] E. Coronado, M. Giménez-Marqués, C.J. Gómez-García, G.M. Espallargas, Dynamic magnetic materials based on the cationic coordination polymer [Cu(btix)2]n2n+ [btix = 1,4-bis(triazol-1- ylmethyl)benzene]: Tuning the structural and magnetic properties through anion exchange, Inorg. Chem. 51 (2012) 12938–12947. doi:10.1021/ic302066e.

[17] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. Sect. A Found. Crystallogr. 64 (2007) 112–122.

doi:10.1107/S0108767307043930.

[18] G.M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, Acta Crystallogr. Sect. A Found. Adv. 71 (2015) 3–8. doi:10.1107/S2053273314026370.

[19] O. V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program, J. Appl. Crystallogr. 42 (2009) 339–341. doi:10.1107/S0021889808042726.

[20] X. Meng, Y. Liu, Y. Song, H. Hou, Y. Fan, Y. Zhu, Novel Zn (II) and Pb (II) coordination networks with large circuits: Synthesis, crystal structures and self-focusing effects, Inorganica Chim. Acta. 358 (2005) 3024– 3032. doi:10.1016/j.ica.2005.03.045.

[21] L. Yang, D.R. Powell, R.P. Houser, Structural variation in copper(I) complexes with pyridylmethylamide ligands: Structural analysis with a new four-coordinate geometry index, τ<inf>4</inf>, Dalt. Trans. (2007) 955–964. doi:10.1039/b617136b.

[22] E. Coronado, M. Giménez-Marqués, G. Mínguez Espallargas, Combination of magnetic susceptibility and electron paramagnetic resonance to monitor the 1D to 2D solid state transformation in flexible metal-organic frameworks of Co(II) and Zn(II) with 1,4-bis(triazol-1-ylmethyl)benzene, Inorg. Chem. 51 (2012) 4403–4410. doi:10.1021/ic300276q.

[23] L.C. Chen, S.M. Huo, H.Z. Chen, Y.Q. Yang, R.H. Zeng, Poly[μ-aquadiaqua(μ 3-1H-benzimidazole-5-carboxylato- κ 3 N 3:O,O′)(μ 2-1H- benzimidazole-5-carboxylato-κ 3 N 3:O:O′)- μ 5-sulfato-μ 4-sulfatotricadmium], Acta Crystallogr. Sect. E Struct. Reports Online. 67 (2011). doi:10.1107/S1600536811034477.

[24] X.M. Hao, G. Chen, C.S. Gu, J.W. Liu, The two-dimensional coordination polymer poly[di-aqua-(μ 2 -1H- imid-azo[4,5-f][1,10]phenanthroline)-μ 4 -sulfato-μ 3 -sulfato-dicadmium(II)], Acta Crystallogr. Sect. C Struct. Chem. 70 (2014) 770–772. doi:10.1107/S2053229614015514.

[25] T. Zhang, J. Lu, Poly[μ2-hydroxido-μ4-sulfato-neodym-ium(III)], Acta Crystallogr. Sect. E Struct. Reports Online. 64 (2008) 889–892. doi:10.1107/S1600536808021818.